ДОКЛАДЫ
АКАДЕМИИ НАУК СССР

PROCEEDINGS OF THE ACADEMY OF SCIENCES

OF THE USSR

Chemistry Section

(DOKLADY AKADEMII NAUK SSSR)

IN ENGLISH TRANSLATION

VOL. 115 NOS. 1-6

CONSULTANTS BUREAU, INC.

227 WEST 17TH STREET, NEW YORK 11, N. Y.

an agency for the interpretation of international knowledge

SOVIET RESEARCH IN CRYSTALLOGRAPHY

Crystallography is a field in which the Russians have been extremely active for many years. This is exemplified by the fact that they publish a journal, Kristallografiia, devoted entirely to articles on this subject. However, many additional articles on crystallographically interesting subjects are scattered throughout the vast Russian chemical literature. As a service to crystallographers, we are publishing as a collection the 112 articles which have been selected by a crystallographer, as the most important in all issues of Russian chemical journals translated by Consultants Bureau, 1949-1955. These journals are: The Journal of General Chemistry; the Bulletin of the Academy of Sciences, Div. Chem. Sci.; the Journal of Analytical Chemistry; the Journal of Applied Chemistry. This Collection, No. 5 in a series being published in various specialized fields, is described directly below:

SOVIET RESEARCH IN CRYSTALLOGRAPHY

IN ENGLISH TRANSLATION

COLLECTION NO. 5

PART 1. Covers compound formation, and reaction studies in complex systems; transformation, solubility, and phase diagrams; metals systems and their reactions.

78 reports, 493 pages, $100.00

PART 2. (More theoretical.) Covers: Structure determination, and structural change; experimental techniques and research methods; structure-sensitive properties; crystal growth and forms; general and theoretical papers.

34 reports, 230 pages, $30.00

Complete, Parts 1 and 2, 112 reports, 723 pages, $115.00

Individual papers available, $7.50 each

CONSULTANTS BUREAU, INC.

227 WEST 17TH STREET, NEW YORK 11, N. Y. ALGONQUIN 5-0718

PROCEEDINGS OF THE ACADEMY OF SCIENCES OF THE USSR

(DOKLADY AKADEMII NAUK SSSR)

Section: CHEMISTRY

Volume 115, Issues 1-6

July-August, 1957

Editorial Board:

Acad. L. A. Artsimovich, Acad. A. G. Betekhtin, Acad. S. A. Vekshinsky,

Acad. A. N. Kolmogorov (Asst. to Editor in Chief), Acad. A. L. Kursanov,

Acad. S. A. Lebedev, Acad. I. N. Nazarov, Acad. A. I. Nekrasov,

Acad. A. I. Oparin (Editor in Chief), Acad. E. N. Pavlovsky, Acad. L. I. Sedov,

Acad. N. M. Strakhov, Acad. A. N. Frumkin (Asst. to Editor in Chief)

(A Publication of the Academy of Sciences of the USSR)

IN ENGLISH TRANSLATION

Copyright, 1958

CONSULTANTS BUREAU, INC.

227 West 17th Street

New York 11, N. Y.

Printed in the United States

Annual Subscription	$95.00
Single Issue	20.00

Note: The sale of photostatic copies of any portion of this copyright translation is expressly prohibited by the copyright owners. A complete copy of any article in this issue may be purchased from the publisher for $5.00.

SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.-Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. - Publisher.

PROCEEDINGS OF THE ACADEMY OF SCIENCES OF THE USSR

Section: CHEMISTRY

Volume 115, Issues 1-6

July-August, 1957

TABLE OF CONTENTS

	Page	Russian Issue	Russian Page
1. The Alkylation of α- and β-Naphthols with Acetylene. V. L. Valser	663	1	91
2. The Distribution of Small Quantities of Carbon in Alloyed Iron. A. S. Zavyalov and B. I. Bruk	667	1	94
3. The Polymerization of Some Compounds Containing Two Isopropenyl Groups. Yu. V. Mitin and N. A. Glukhov	671	1	97
4. The Reaction of Cerium with Hydrogen. V. I. Mikheeva and M. E. Kost	675	1	100
5. Concomitant Decarboxylation During Autoxidation of Isopropylbenzene in Admixture with Fatty Acids. N. N. Mitskevich, T. I. Soroko and B. V. Erofeev	679	1	103
6. Synthesis and Properties of Mono-, Di- and Tri-p-tolylalkyl Silanes. N. S. Nametkin, A. V. Topchiev, Gu Chan-Li and N. A. Leonova	685	1	107
7. Dependence of the Relative Heat Resistance on Composition in the System Cu-Ni-Si. I. I. Novikov and L. I. Dautova	689	1	110
8. Properties of α-Cellulose Derived from Fossil Pinewood of Millenial Age. A. I. Skrigan, A. M. Shirbko and R. G. Zhbankov	693	1	114
9. Electron Paramagnetic Resonance in some Chromium-Containing Aromatic Compounds of Sandwich Structure. Yu. D. Tsvetkov, V. V. Voevodsky, G. A. Razuvaev, Yu. V. Sorokin and G. A. Domrachev	697	1	118
10. Contribution to the Question of Conjugation in Butadiene. M. I. Batuev	701	2	291
11. Polymorphism of Thallium Bisulfate. N. I. Bashilova	705	2	295
12. On the Two Courses of Reaction in the Dehydrochlorination of Lower Alkylene Chlorohydrins. P. V. Zimakov and L. M. Kogan	707	2	297
13. Hydrogenation of Vinylcyclopropane and 1-Methyl-1-isohexenylcyclopropane in the Presence of Platinum and Palladium. B. A. Kazansky, M. Yu. Lukina and L. G. Salnikova	711	2	301
14. Alkyl Esters of Ethylthioarsinous [Ethylthiolarsonous] Acid. Gilm Kamal and N. A. Chadaeva	717	2	305
15. On the Formation of Polymeric Hydrocarbons by the Decomposition of Aliphatic Diazo Compounds. V. V. Korshak and V. A. Sergeev	721	2	308
16. Halochromism of Phenyl- and Cyclohexylcarbinols. V. F. Lavrushin and N. N. Verkhovod	725	2	312

PROCEEDINGS OF THE ACADEMY OF SCIENCES OF THE USSR

July-August, 1957

TABLE OF CONTENTS

(continued)	Page	Russian Issue	Russian Page
17. Beta-Cyanovinyl Ketones. A. N. Nesmeyanov and M. I. Rybinskaya	729	2	315
18. Transformations in Ternary Solid Solutions Based on Ni_3Fe. M. P. Ravdel and Ya. P. Selisky	733	2	319
19. Investigation of Aqueous Solutions of Sodium Paratungstate. Vikt. I. Spitsyn and G. N. Pirogova	737	2	322
20. Synthesis of Some Alkylhalosilanes and Silicohydrocarbons. A. V. Topchiev, N. S. Nametkin and T. I. Chernysheva	741	2	326
21. Catalytic Hydrogenolysis of Sylvan Over Various Catalysts. N. I. Shuikin and I. F. Belsky	745	2	330
22. The Binding of Lime in Calcium Hydrosilicate Under Normal Conditions. V. F. Abrosenkova, G. I. Logginov and P. A. Rebinder	749	3	509
23. Tautomerism of Diphenyl Phosphite. M. I. Kabachnik and Yu. M. Polikarpov	753	3	512
24. Complex Formation and Chain Structure in the Polymerization of Divinyl with Butyllithium. V. A. Kropachev, B. A. Dolgoplosk and N. I. Nikolaev	759	3	516
25. The Influence of Substituents on the Strength of Ferrocenecarboxylic Acids. Nik. A. Nesmeyanov and O. A. Reutov	763	3	518
26. Synthesis and Dehydration of Unsaturated Silicon-Containing Alcohols. A. D. Petrov, L. L. Shchukovskaya, S. I. Sadykh-Zade and Yu. P. Egorov	767	3	522
27. Tautomerism of Arylazotropolones. M. M. Shemyakin, F. A. Mendelevich, A. M. Simonov and V. B. Petrinska	773	3	528
28. Kinetics of Catalytic Dehydrogenation of Isopropyl Alcohol in Presence of Transition Metals of the Fourth Period. A. A. Balandin and P. Teteni	777	4	727
29. Catalysts on the Basis of Alkyl Magnesium Halides and Titanium Tetrachloride for the Synthesis of Amorphous and Crystalline Polymers from α-Olefins and Dienes. B. A. Dolgopolsk, L. M. Romanov, V. L. Erusalimsky and V. Ya. Bogomolnyi	781	4	731
30. Thermal Telomerization of Olefins with Silanes Containing Si-H Bond. A. N. Nesmeyanov, R. Kh. Freidlina and E. Ts. Chukovskaya	785	4	734
31. The Association of Organolithium Compounds of the Aliphatic Series in Hydrocarbon Solutions. K. B. Piotrovsky and M. P. Ronina	789	4	737
32. The Chemical Composition of Gasolines from Thermal and Catalytic Cracking. E. G. Iskhakova, T. V. Fedorova, T. N. Buturlova and N. N. Chekalova	793	4	740

TABLE OF CONTENTS

(continued)	Page	Russian Issue	Russian Page
33. The Mechanism for the Oximation of Cyclohexanone with Sodium Hydroxylamine Monosulfonate. E. N. Zilberman and M. M. Smirnova	797	5	927
34. Study of the Nitration of Isopropylcyclohexane with Nitric Acid. A. V. Topchiev, S. D. Mekhtiev and A. Sh. Novruzova	801	5	931
35. The Reaction of the Intermediate Products of the Arbuzov Rearrangement with Amines. A. E. Arbuzov and N. N. Sazonova	805	6	1119
36. On the Mechanism of the Thermal Decomposition of Cellulose Under Vacuum and the Formation of 1,6-Anhydro-1,5-Glucopyranose–Levoglucosan. O. P. Golova, A. M. Pakhomov, E. A. Andrievskaya and R. G. Krylova	809	6	1122
37. Experimental Basis for a Chain Mechanism of the Heterogeneous-Catalytic Hydropolymerization of Olefins under the Influence of Carbon Monoxide and Hydrogen. N. I. Ershov and Ya. T. Eidus	813	6	1126

BLANK
PAGE

THE ALKYLATION OF α- AND β-NAPHTHOLS WITH ACETYLENE

V. L. Vaiser

(Presented by Academician A. V. Topchiev, March 15, 1957)

Alkylation was performed in a reactor containing a solution of the naphthol in 50 ml ethyl or butyl alcohol and $H_3PO_4 \cdot BF_3$ + 1 g of mercuric oxide. Acetylene was passed in from a cylinder at a controlled rate. The mass obtained at the end of the reaction was suction-filtered on a Buchner funnel and the crystals of alkylate were washed with butyl alcohol. Results of the experiments are presented in Table 1.

TABLE 1

Alkylation of β-Naphthol

Experiment No.	Naphthol, ml	Catalyst		Temperature, °C	Acetylene addition rate, liters/hr	Duration of reaction (hours)	Yield of alkylate	
		ml	weight-% in reaction mixture				in g	in % of theory (on naphthol taken)
1	20	5	14	65—70	2	3	8.5	41
2	20	5	14	65—70	2	3	8.7	42
3	20	5	14	75—80	2	1.5	9.5	46
4	20	5	14	65—70	2	1.5	6.5	32
5	20	5	14	21—25	2	1.5	2	10
6	20	5	14	105—110	2	1.5	8	39
7	20	5	14	75—80	2	1.5	9.5	44
8	20	5	14	65—70	2	1.5	7	34
9	20	5	14	21—25	2	3	3	15
10	20	2.5	7	65—70	2	3	4	20
11	20	1.25	4	65—70	2	3	1	5
12	20	10	24	65—70	2	3	9.5	46
13	20	10	24	65—70	2	3	6	30
14	15	5	15	65—70	2	3	6	39
15	10	5	16	65—70	2	3	7	68
16	5	5	18	65—70	2	3	2.8	55
17	20	5	14	65—70	2	3	8.6	42
18	32	—	—	65—70	2	3	13.5	41
19	39	—	—	65—70	2	3	9.5	24
20	50	—	—	65—70	2	3	10	20

Notes. 1. In experiments 5 to 8 the solvent was n-butyl alcohol; in all the remaining experiments it was ethyl alcohol. 2. In experiments 18 to 21, 20 g naphthol was charged into the reactor together with the catalyst left over from the preceding experiment and the unconsumed naphthol.

Experiments 1, 2 and 17 (in which the yields of alkylate were respectively 41, 42 and 42%) as well as experiments 4, 6, 5 and 9 were performed under identical conditions of temperature, catalyst concentration, etc. The results are seen to be reproducible irrespective of whether ethyl or butyl alcohol was the solvent.

Data for the yield of alkylate as a function of the catalyst concentration under otherwise identical conditions are plotted in Fig. 1.

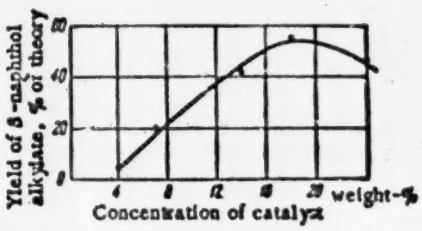


Fig. 1. Yield of alkylate of β-naphthol as a function of the catalyst concentration.

The optimum yield of alkylate concentration of 68% at a catalyst concentration of 18% in the reaction mixture at a temperature of 65-70°. Data for the yield of alkylate as a function of the temperature under otherwise identical conditions are plotted in Fig. 2. The optimum temperature was 75-80° with a catalyst concentration of 14%.

An increase in the rate of introduction of the acetylene from 2 liters/h to 4 liters/h only lowers the yield of alkylate by 10%.

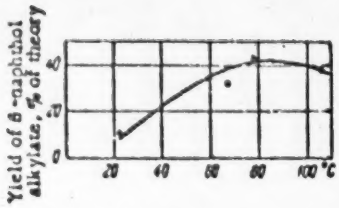


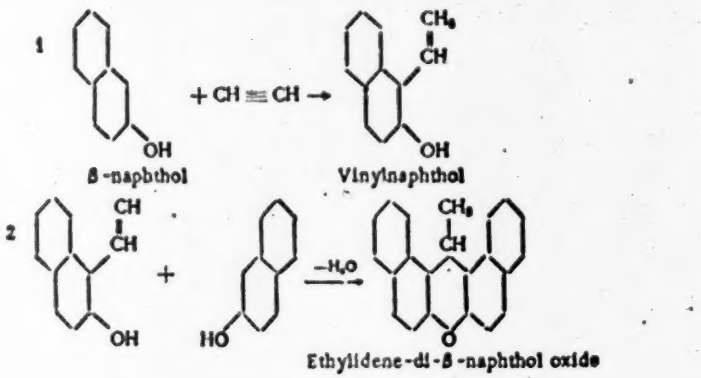
Fig. 2. Yield of β-naphthol alkylate as a function of the temperature.

The alkylate obtained is sparingly soluble in benzene, readily soluble in acetone, acetic acid, ether and chloroform; it dissolves in carbon tetrachloride and n-heptane when heated; it is insoluble in caustic alkali and weak sulfuric acid. M. P. 173 °C.

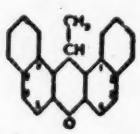
Found (in %): C 89.3; H 5.5; O 5.2. For $C_{22}H_{16}O$, calculated (in %): C 89.2; H 5.4; O 5.4.

Molecular weight 296-301. $C_{22}H_{16}O$ calculated, molecular weight 296. Tserevitinov determination revealed the absence of hydroxyl groups.

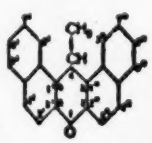
Taking into account the results of our experiments on the alkylation of phenol [1,2] and cresols [3] under similar conditions, we consider the alkylate to be ethylidene-di-β-naphthol oxide, formed according to the scheme.



This heterocyclic compound can be regarded as a xanthene derivative, 9-methyl-1,2,7,8-dibenzoxanthene

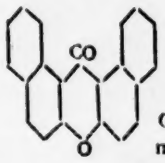


or as a pyran derivative, 4-methyl-[di-naphtho-2"1";2,3;1'2';5,6]-pyran.



Such a compound with m.p. 173° was prepared by Claisen [4] by condensation of β-naphthol with paraldehyde in presence of HCl.

Oxidation of the alkylate with chromic oxide gave crystals with m.p. 194°. The oxidation process involves conversion of the radical to the carbonyl group with formation of the corresponding ketone:



$C_{21}H_{12}O_2$ — dinaphtho-γ-pyrone
mol. wt. 296

Wenzke and Nieuwland [5] carried out the condensation of acetylene with naphthol in 95% alcoholic solution in presence of concentrated sulfuric acid and mercury salts. They failed, however, to isolate any crystals from the solution. These authors carried out the reactions with α- and β-naphthols for 10 days and obtained a small quantity of crystals with m.p. 173°. They claimed to obtain an acetal when using β-naphthol and ethylidene-dinaphthol oxide when using α-naphthol. Unfortunately the authors do not submit adequate evidence for their claim.

We alkylated α-naphthol under the same conditions as for β-naphthol. The alkylate was insoluble in benzene and camphor, which hindered determination of the molecular weight.

LITERATURE CITED

[1] V. L. Vaiser and A. M. Polikarpova, Proc. Acad. Sci. USSR, 97 No. 4 (1954).

[2] V. L. Vaiser, Proc. Acad. Sci. USSR, 103, No. 5 (1955).

[3] V. L. Vaiser and A. M. Polikarpova, Proc. Acad. Sci. USSR, 108, No. 5 (1956).*

[4] L. Claisen, Lieb. Ann., 237, 270 (1887).

[5] N. N. Wenzke and J. A. Nieuwland, J. Am. Chem. Soc., 46, 177 (1924).

I. M. Gubkin Institute of Petroleum,
Moscow

Received June 16, 1958

* Original Russian pagination. See C. B. Translation.

BLANK
PAGE

THE DISTRIBUTION OF SMALL QUANTITIES OF CARBON IN ALLOYED IRON

A. S. Zavyalov and B. I. Bruk

(Presented by Academician G. V. Kurdyumov, January 10, 1957)

The problem of the distribution of alloying elements, especially carbon, in the microscopic portions of the α- and γ-solid solution in iron alloys is receiving ever greater attention in metallurgical investigations but has not yet been conclusively clarified by experiment.

In the present work the nature of the distribution of carbon in alloyed iron was studied by the method of autoradiography using the radioactive isotope C^{14}. The value of this method for study of the distribution of some elements in iron and ferrous alloys has been demonstrated in a series of papers [1-7].

A study was made of low-carbon ferrous alloys containing (separately) chromium, nickel, silicon and molybdenum. Compositions are given in Table 1.

TABLE 1

System investigated	Chemical composition, %					
	C	Cr	Ni	Mn	Si	Mo
Iron-chromium	0.05	4.6	–	0.10	0.10	–
Iron nickel	0.04	0.08	4.8	trace	0.11	–
Iron-silicon	0.03	0.09	–	trace	4.4	–
Iron-molybdenum	0.03	0.08	–	0.08	0.10	12.5

Radioactive carbon was introduced into the alloys by cementation method in a medium of radioactive barium carbonate. Since the source of the radiocarbon was solely barium carbonate without addition of the carbon, the total content of carbon in the cemented specimens did not rise above their original content of 0.03-0.05%. Penetration of radioactive carbon (designated arbitrarily by C*) from the $BaCO_3$ into the steel was effected by isotopic exchange, evidently according to the following scheme:

$$2BaC^*O_3 \rightarrow 2BaO + 2C^*O_2$$

$$2C^*O_2 + 2C \rightarrow 2C^*O + 2CO$$

From the steel

$$2C^*O + 2CO \rightarrow C^*O_2 + CO_2 + \underbrace{C^* + C}$$

Into the steel

The radioactive specimens were radiographed after they had been subjected to the specified thermal treatment. The MR type of nuclear film of the Scientific Institute of Motion Picture Photography was used for the exposures.

Examination of the autoradiograms of the annealed alloys (Fig. 1a,4a) reveals that a characteristic feature of the annealed state is the very conspicuous irregularity of distribution of carbon at the grain boundaries; this is particularly marked in iron-silicon and iron-molybdenum alloys in which the carbon is mainly concentrated at the grain boundaries.

The autoradiograms of alloys quenched in water from a temperature of 1200° (Fig. 1b-4b) have a perfectly uniform darkening at the specified magnification; a similar picture was also obtained after quenching from a temperature of 950°. This indicates that at temperatures of 900 and 1200° these alloys do not become enriched with carbon at the austenitic grain boundaries (in the case of Fe-Cr and Fe-Ni alloys)or at the ferritic grain boundaries (in the case of Fe-Si and Fe-Mo alloys).

A certain general tendency is observed with all the alloys in the quenched annealed state in respect to the character of the distribution of carbon (uniformity of the carbon after quenching and its redistribution after annealing). On the other hand, tempering of the quenched alloys (590° for 10 hours) leads to two groups of alloys differing markedly in respect to the degree of irregularity of distribution of carbon: the iron-chromium alloy (Fig. 1c), exhibiting no tendency towards redistribution of carbon, and alloys of iron with nickel, silicon and molybdenum (Figs. 2c-4c) in which the tempering led to much redistribution of carbon and its enrichment at the grain boundaries.

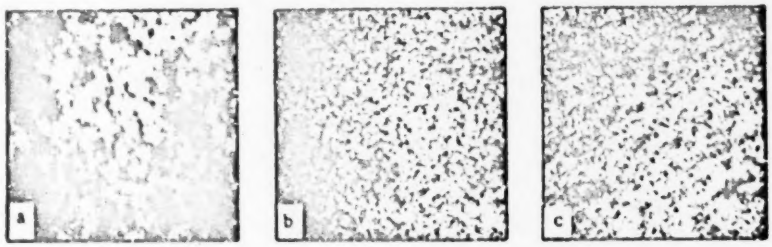


Fig. 1. Autoradiograms of iron alloy containing 4.8% chromium; x 65; a = annealed at 970°, 50 hours; b = quenched in water from 1200°; c = tempered at 590°, 10 hours.

Fig. 2. Autoradiograms of iron alloy containing 4.8% nickel; x 65; a = annealed at 970°, 50 hours; b = quenched in water from 1200°; c = tempered at 590°, 10 hours.

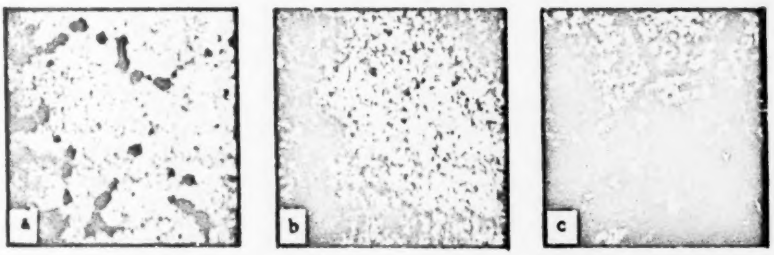


Fig. 3. Autoradiograms of iron alloy containing 4.4% silicon; x 65; a = annealed at 970°, 50 hours; b = quenched in water from 1200°; c = tempered at 590°, 10 hours.

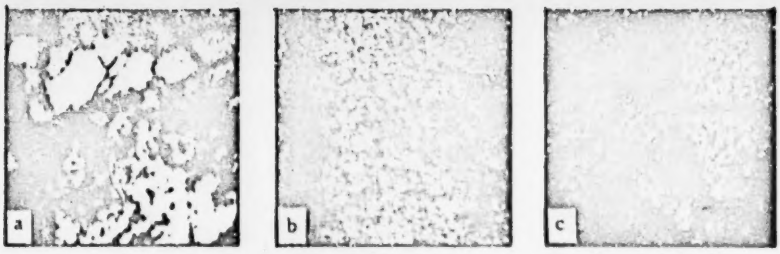


Fig. 4. Autoradiograms of iron alloy containing 12.5% molybdenum; x 65; a = annealed at 970°, 50 hours; b = quenched in water from 1200°; c = tempered at 590°, 10 hours.

These data clearly confirm the view that carbide-forming elements are able to retain carbon in ferrite up to high tempering temperatures and that the processes of segregation of carbon by non-carbide-forming elements* [8] are intensified.

Clear illustration is also provided of the correctness of the view that silicon is more effective than nickel as an intensifier of the processes of redistribution and separation of carbon [8]. A comparison of the autoradiograms of tempered specimens of iron-nickel (Fig. 2c) and iron-silicon (Fig. 3c) alloys indicates that in the second case the effect of the tempering is to displace the carbon more intensively towards the grain boundaries than in the first case.

The uniform darkening of the autoradiogram of the tempered iron-chromium alloy (Fig. 1c) indicates that at a temperature higher than AC_3 the chromium is uniformly distributed at the grain boundaries. Indeed, if irregular distribution of chromium had occurred in the austenite, then the tempering after the quenching should have caused the carbon to be displaced to sites enriched in this element due to the differing velocities of diffusion of carbon and chromium in ferrite [6].

The fact that migration of carbon did not take place in the iron-chromium alloy as a result of tempering (Fig. 1c) testifies to the uniform (in relation to the grain boundaries) distribution of chromium in austenite at 1200°.

By analogy with the Fe-Cr alloy, it might be expected that in the Fe-Mo alloy the character of the distribution of the carbon would also not change as a result of tempering after quenching. Actually, however, in the tempered iron-molybdenum alloy there is a more clearly marked concentration of carbon along the grain boundaries (Fig. 4c).

The reason for this change is to be sought in the phase composition of the alloy concerned. If the concentration of one of the elements in a binary system exceeds its limiting solubility in the solid solution, then the excess of that element separates in the form of a solid phase predominantly at the grain boundaries of the solid solution. If the system also contains a small amount of a third element, either the latter will diffuse to the grain boundaries if the strength of its bond with the atoms of the separated element is greater then the strength of the bond with the atoms of the solvent element, or it will diffuse into the interior of the grain if the strength of the bond with the atoms of solvent exceeds the strength of the bond with the atoms of the segregated element [8].

In the case of the iron-molybdenum alloy under consideration (containing 12.5% Mo), the presence of a certain quantity of ϵ-phase in the structure side by side with the α-phase is unavoidable, since the maximum concentration of molybdenum in the α-phase is 8% even at 600°. Since the lowest concentration of molybdenum in the ϵ-phase is 50%, the concentration of this phase at the boundaries of a ferritic grain must of course bring about diffusion of carbon towards it during the process of tempering due to the known affinity between molybdenum and carbon.

Thus the process of concentration of carbon at the boundaries of the ferritic grain in Fe-Si alloys (Fig. 3c) and Fe-Mo alloys (Fig. 4c) gives the same radiographic effect but occurs for different reasons; in the Fe-Si alloy

* The question of the probable causes of separation of carbon during temperturing of the iron-molybdenum alloy will be considered below.

the carbon is displaced towards the boundaries of the grain by the silicon uniformly distributed in the alloy; in the Fe-Mo alloy (containing 12.5% molybdenum), the carbon diffuses towards the grain boundaries due to separation at these boundaries of excess phase enriched with molybdenum.

LITERATURE CITED

[1] S. Z. Bokshtein, T. I. Gudkova, S. T. Kishkin, and L. M. Moroz, Works Lab., No. 4 (1955).

[2] S. T. Kishkin, and S. Z. Bokshtein, Report of Soviet Delegation to the Geneva International Conference on the Peaceful Uses of Atomic Energy, Acad. Sci. Press, 1955.

[3] I. R. Kryanin, S. I. Smolensky, M. A. Studnits and G. I. Babushkina, Metallurgy and Metal Working, No. 3 (1956).

[4] S. T. Kishkin, S. Z. Bokshtein, L. M. Moroz and T. I. Gudkova, Proc. Acad. Sci. USSR, 101 No. 4 (1955).

[5] M. A. Studnits and O. T. Matyuchkov, Metallurgy and Metal Working, No. 6 (1955).

[6] S. F. Yuryev and B. I. Bruk, Proc. Acad. Sci. USSR, 104, No. 4 (1955).

[7] B. I. Bruk, Welding Industry USSR, No. 11 (1955).

[8] A. S. Zavyalov, Theory of alloying and heat treatment of steel, 1943.

Central Research Institute of the Ministry
of the Shipbuilding Industry of the USSR

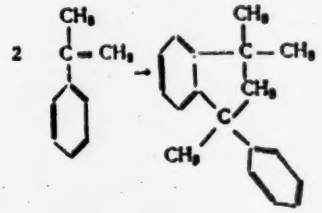
Received January 2, 1957

THE POLYMERIZATION OF SOME COMPOUNDS CONTAINING TWO ISOPROPENYL GROUPS

Yu. V. Mitin and N. A. Glukhov

(Presented by Academician V. A. Kargin, April 17, 1957)

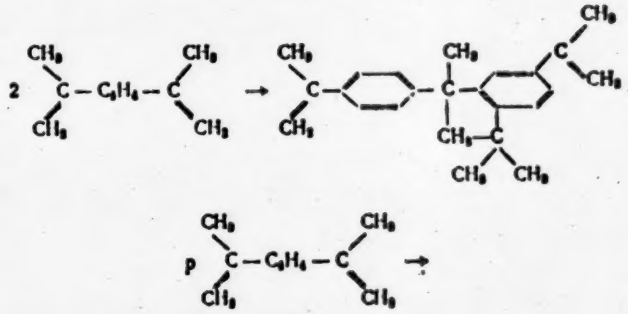
In a study of the dimerization of α-methylstyrene under the influence of catalysts of an ionic type ($SnCl_4$, $TiCl_4$, $AlCl_3$) it was shown that at elevated temperature (70-100°) there is exclusive formation of a dimer which is a saturated, crystalline product [1,2]. Direct synthesis showed conclusively [2] that the saturated dimer was 1,1,3-trimethyl-3-phenylindane.

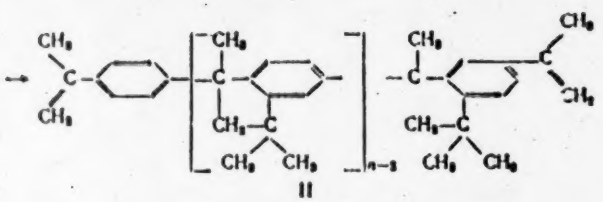


I

Similar products of dimerization are also formed by other ring-substituted α-methylstyrenes. Consequently, α-methylstyrene functions as a monofunctional compound under certain conditions.

It was of interest to investigate the behavior of compounds containing two isopropenyl groups under conditions analogous to the conditions of formation of the saturated dimer of α-methylstyrene. A series of bifunctional compounds was therefore investigated with the objective of preparing linear polymers containing benzene rings in the principal chain. It might have been expected that under certain conditions the bifunctional compound, e.g. 1,4-diisopropenylbenzene, would react by the following route:

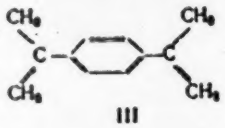




II

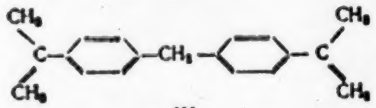
We synthesized and characterized the following compounds:

1,4-diisopropenylbenzene [3]



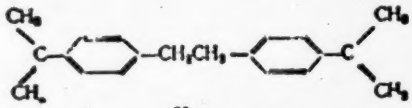
III (m.p. 64-64.5°)

4,4'-diisopropenyldiphenylmethane



IV (m.p. 54.5-55°)

4,4'-diisopropenyldiphenylethane

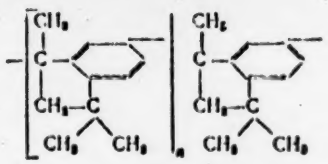


V (m.p. 124-124.5°)

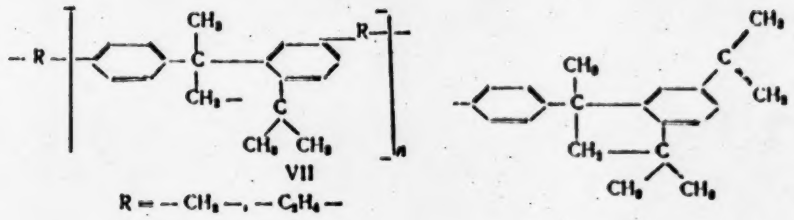
The prepared compounds were subjected to polymerization in toluene solution in presence of $SnCl_4$ and HCl as cocatalyst. In all cases the resultant polymers were soluble in benzene and its homologs, in carbon tetrachloride, carbon disulfide and a few other solvents, and insoluble in alcohols. After reprecipitation the polymers were obtained in the form of white powders. Some properties of the polymers are listed in Table 1.

TABLE 1

Monomer	Properties of polymer		
	[η]	M	Solubility
III	0.07	$7.0 \cdot 10^3$	in C_6H_6, CCl_4, CS_2, hexane
IV	0.30	—	in C_6H_6, CCl_4, CS_2
V	0.70	$7.8 \cdot 10^3$	in C_6H_6, CCl_4, CS_2



VI



VII

R = — CH_2 —, — C_2H_4 —

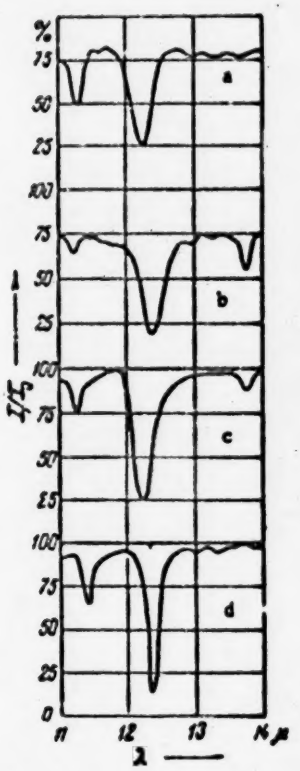
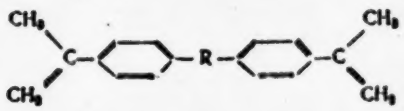


Fig. 1. Infrared absorption spectra (4.5% in ISP-14-B apparatus, NaCl prism): a) poly-1,4-diisopropenylbenzene; b) poly-4,4'-diisopropenyldiphenylmethane; c) poly-4,4'-diisopropenyldiphenylethane; d) 1,3,6-trimethylindane.

The elementary composition of all the prepared polymers exactly coincides with that of the corresponding starting monomers. The polymers are saturated and do not add on bromine. The structure of the polymer of 1,4-diisopropenylbenzene may be represented by formula VI, and the structure of the polymers of 4,4'-diisopropenyldiphenylmethane and 4,4'-diisopropenyldiphenylethane by formula VII.

Due to the exceptional resistance of the polymers to oxidative and thermal attack, it was impossible to obtain any pure products of oxidation or breakdown. However, the similarity between the infrared spectra of the polymers and of 1,3,6-trimethylindane [4] (the latter selected as a model compound) supports structures VI and VII. Examinations of the optical properties of solutions of polymers (carried out in the laboratory of Prof. V. N. Tsvetkov by S. Ya. Magarink to whom the authors convey their thanks) convincingly show that the benzene ring is in the principal chain of the polymer [5].

It has thus shown that under specific conditions it is possible to obtain linear polymers on the basis of compounds of the type of



where R is the atom or group of atoms not reacting (in the broad sense of the word) with catalysts of the ionic type.

The authors convey their deep gratitude to Prof. M. M. Koton and V. V. Nikitin for valuable advice and help in the work.

LITERATURE CITED

[1] H. Staudinger and F. Breusch, Ber., 62, 452 (1929).

[2] E. Bergmann, H. Taubald and H. Weiss, Ber., 64, 1403 (1931).

[3] M. T. Bogert and C. P. Harris, J. Am. Chem. Soc. 41, 1682 (1919).

[4] Ph. Theysie and G. Smets, J. Polym. Sci. 20, 351 (1956).

[5] V. N. Tsvetkov and S. Ya. Magarik, Proc. Acad. Sci. USSR, 115, No. 5 (1957).*

Institute of High-Molecular Compounds of the
Academy of Sciences of the USSR

Received February 8, 1957

* Original Russian pagination. See C. B. Translation.

THE REACTION OF CERIUM WITH HYDROGEN

V. I. Mikheeva and M. E. Kost

(Presented by Academician I. I. Chernyaev, January 12, 1957)

When metallic cerium is heated in a hydrogen atmosphere to 250-300°, it begins to absorb hydrogen energetically with formation of a hydride of variable composition [1-3].

The question of the existence of a hydride of cerium with the stoichiometric composition CeH_3 was posed in 1913 by I. I. Zhukov [4,5] on the basis of a study of the curve of the dissociation pressures of the hydride. Later the existence of the hydride CeH_3 was confirmed by the calorimetric investigations of K. Fredenhagen [6,7]. These later investigations also reported the preparation of a hydride CeH_3 from mischmetall (an alloy of rare earths containing about 50% Ce [6] as well as from pure cerium [7].

The starting metal in our work was cerium obtained from the Institute of Rare Metals containing 97% Ce and 2.9% Nd and Pr according to the spectral analysis. The amount of hydrogen taken up by cerium was determined by three parallel methods: 1) from the amount of hydrogen absorbed (fall of pressure in the system); 2) from the increase in weight of the sample of metallic cerium; 3) from the volume of hydrogen released on dissolving the hydride in dilute hydrochloric acid. The determinations were accurate to within ± 2% of the amount determined.

A sample of metal weighing 0.1-3 g was carefully surface-cleaned in a strong stream of dry carbon dioxide and placed in a quartz tube connected to a vacuum system. After pumping out with a diffusion pump to 10^{-4} mm mercury column, a furnace was moved over the tube and the temperature was maintained constant to ± 5°.

Hydrogen thoroughly purified from oxygen and water vapor was introduced into the system after 5 minutes, and the pressure drop was measured with the help of a mercury manometer. After absorption had ceased, the excess of hydrogen was pumped out and the product was cooled to room temperature in vacuum. The hydride was extracted in a stream of dried carbon dioxide as a precaution against burning of the hydride in contact with air.

During the process of hydrogenation it was observed that, contrary to the reports in the literature [2,3,8], hydrogenation of cerium takes place at room temperature without preliminary thermal treatment of the specimen if the starting substances have been thoroughly purified. The composition of the product then fluctuates between CeH_3 and $CeH_{3.4}$. Hydrogenation of cerium at increased pressure (up to 14 atm.) revealed that the composition of cerium hydride does not depend upon the hydrogen pressure.

The curves of duration of hydrogenation versus hydrogen pressure drop (Fig. 1) differ in character at different temperature ranges. At low temperatures hydrogenation is preceded by an appreciable induction period which disappears above 200°. Figure 2 is a plot of duration of hydrogenation (up to saturation) as function of temperature for identical weighed quantities of cerium. Up to 200° and higher than 700° the speed of hydrogenation, in contrast to that in the 300-600° range, increases with rising temperature.

The dependence of the composition of cerium hydride on the temperature was studied with two different experimental regimes. When the excess hydrogen was pumped out after saturation of cerium at each of the given temperatures (Fig. 3, curve 1), the form of the curve of saturation resembles that of curve 2 (obtained by Sieverts and Roell [3] under the same conditions). Experiments based mainly on curve 3 were performed by heating a specimen with the composition CeH_3 at the given temperatures until equilibrium was established.

The composition of the final product was calculated from the volume of gas given off. The form of curve 3 differs markedly from that of curves 1 and 2: it contains two horizontal lengths corresponding to the composition CeH_3 and CeH_2. The temperature regions of their existence correspond to the descending branches of the curve of Fig. 2, i.e., the rate of formation of these hydrides increases with rising temperature. At the same time the formation of hydrides of variable composition (300-700°) is accompanied by a fall in velocity of reaction with rising temperature, which is possibly bound up with the solubility of hydrogen in CeH_2.

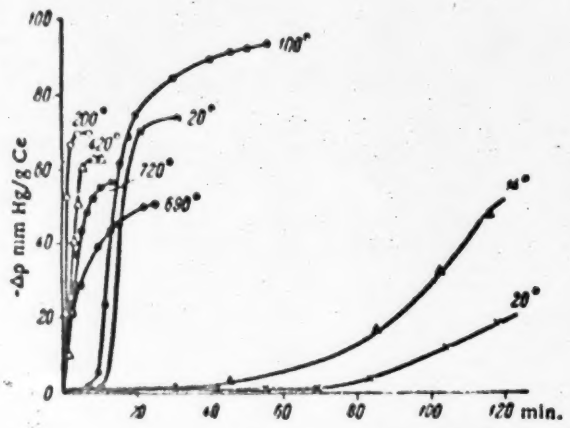


Fig. 1. Isotherms of absorption of hydrogen by cerium.

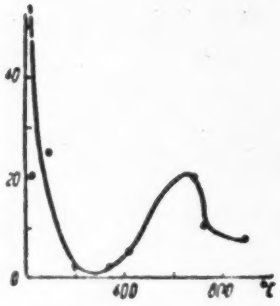


Fig. 2. Period of absorption of hydrogen by cerium.

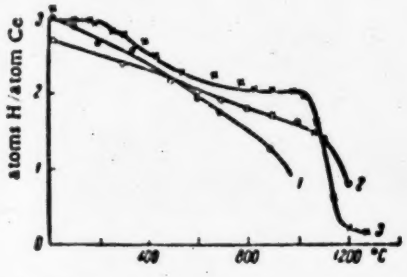


Fig. 3. Dependence of the composition of cerium hydride on the temperature.

The following conclusions can be drawn from the data of the present work:

1. Hydrogenation of metallic cerium under conditions of careful purification of the starting substances takes place at room temperature without preliminary thermal treatment of the specimen of cerium.

2. A hydride of the composition CeH_3 - $CeH_{3.46}$ is obtained when hydrogen is absorbed at room temperature (14-21°) irrespective of the hydrogen pressure.

3. The curve of hydride composition as a function of temperature and the curves of hydrogenation velocity confirm the formation of definite hydrides CeH_3 and CeH_2 and the existence of phases of variable composition between CeH_3 and $CeH_{3.46}$.

LITERATURE CITED

[1] W. Muthman, K. Kraft, Lieb. Ann., 325, 263 (1902).

[2] A. Sieverts, G. Müller-Goldegg, Zs. anorg. allgem. Chem., 131, 65 (1923).

[3] A. Sieverts, E. Roell, Zs. anorg. allgem. Chem., 146, 149 (1925).

[4] I. L. Zhukov, J. Russ. Phys. Chem. Soc., 45, 2073 (1913).

[5] I. L. Zhukov, Bull. Inst. Phys.-Chem. Analysis, 2, 600 (1927).

[6] K. Dialer, Monatsh., 79, 296 (1948).

[7] K. Dialer, W. Rothe, Zs. Elektrochem., 59, 970 (1955).

[8] R. N. Mulford, C. E. Holley, J. Phys. Chem., 59, 1222 (1955).

N. S. Kurnakov Institute of General and Inorganic Chemistry of the Academy of Sciences USSR

Received January 8, 1957

BLANK
PAGE

CONCOMITANT DECARBOXYLATION DURING AUTOXIDATION OF ISOPROPYLBENZENE IN ADMIXTURE WITH FATTY ACIDS

N. N. Mitskevich, T. I. Soroko and Academician of the Acad. Sci. of the White Russian SSR B. V. Erofeev

We showed previously [1,2] that low-temperature autoxidation of resin acids is accompanied by the decarboxylation of these acids. In this connection interest was attached to the possibility of concomitant decarboxylation of carboxylic acids in admixture with hydrocarbons that were being subjected to autoxidation. Experiments on these lines showed that autoxidation of isopropylbenzene in admixture with acetic, butyric, isobutyric and stearic acids is indeed accompanied by decarboxylation of the acids. Thus, in the case of autoxidation of mixtures of hydrocarbons and carboxylic acids the oxidation of the hydrocarbon initiates a linked process of decarboxylation of the acid (using the terminology introduced by N. A. Shilov [3]).

Since autoxidation of hydrocarbons, especially at higher temperatures, can lead to formation of acids which in the course of further autoxidation are subjected to conjoint decarboxylation, an insight into this phenomenon is of definite interest for our understanding of the mechanism of oxidation of hydrocarbons in general.

It should be noted that spontaneous decarboxylation of fatty acids only occurs at temperatures very much higher than those at which we detected conjoint decarboxylation.

Thus, Hurd [4] points out that acetic acid does not break down below the temperature of dark-red heat. According to Bamford and Dewar [5], acetic acid vapor is decomposed with measurable velocity at above 500°. Senderens and Aboulenc [6] found that butyric, isobutyric, propionic and isovaleric acids are stable at up to 460°. In presence of animal charcoal these acids start to break down to an appreciable extent at 330-340°. According to Korshak and Rogozhin [7] the majority of dicarboxylic acids (which decarboxylate more easily than monocarboxylic) only decompose spontaneously at above 200°.

Isopropylbenzene (commercial product from the Voikov Chemical Works) was first fractionated four times over sodium in a glass-packed column, after which it had the following constants: b.p. 149-151°, d_4^{20} 0.860, n_D^{20} 1.4917. Acetic acid (chemically pure product from the Kharkov Chemical Reagent Works) was further purified by freezing [8]. Butyric, isobutyric and stearic acids ("pure") were purified by distillation at atmospheric pressure. Radioactive acetic acid (C^{14} in the carboxyl, obtained through Soyuzreaktivsbyt*) had an activity of 1 mCu/ml. Acetic acid diluted 100.9 times with ordinary acetic acid was used in the experiments. Consequently, the activity of the directly used acetic acid was 0.0099 mCu/ml. Cobalt acetate, used as initiator of autoxidation ("pure" product from the Red Chemical Works), was not subjected to further purification. Analysis showed it to contain 4 molecules of crystal water.

The velocity of autoxidation of mixtures of isopropylbenzene and the acids was investigated in a static system by the method previously described [9] at a temperature of 80.5°. The CO_2 content of the gas phase above the products of the experiment was determined by blowing oxygen through the system and collecting the carbon dioxide in barytes water. In addition, the composition of the gas phase above the products of oxidation was analyzed with the apparatus of the All-Union Thermotechnical Institute.

Radioactive CO_2 in the gaseous products of oxidation was determined by absorption in barytes water and measurement of the radioactivity of the barium carbonate precipitate in a Type B apparatus. The progress of absorption of oxygen is plotted in Fig. 1 as a function of time in experiments with isopropylbenzene without

* As in original — Publisher's note.

and with addition of acetic, butyric, isobutyric and stearic acids. The quantity of acid added was 9.0 to 32.8 mole-%. Cobalt acetate was added in the proportion of $2.1 \cdot 10^{-3}$ mole per mole of isopropylbenzene. As we see from Fig. 1, in presence of acids the velocity of autoxidation of isopropylbenzene increases by approximately the same factor (the amount of oxygen absorbed after 5 hours in presence of any of the acids was over 4 times greater than in the absence of acid). In all of the experiments the initial velocity was the highest and it fell off with progress of the oxidation.

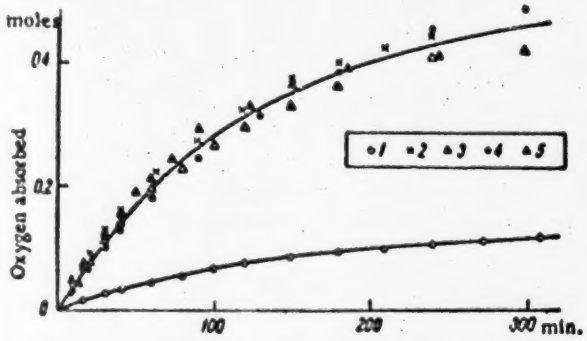


Fig. 1. Kinetic curves of oxidation of isopropylbenzene in presence of fatty acids. Temperature 60.4°, initiator cobalt acetate ($2.1 \cdot 10^{-3}$ mole per mole of isopropylbenzene); 1) pure isopropylbenzene; 2) 32.8 mole-% acetic acid; 3) 9.0 mole-% stearic acid; 4) 31.4 mole-% butyric acid; 5) 31.1 mole-% isobutyric acid.

The influence of the acid concentration on the velocity of oxidation of isopropylbenzene was studied in experiments using various concentrations of isobutyric acid (Table 1).

TABLE 1

Influence of Concentration of Isobutyric Acid on the Velocity of Autoxication of Isopropylbenzene ($14.3 \cdot 10^{-3}$ mole isopropylbenzene; $0.9 \cdot 10^{-3}$ mole cobalt acetate per mole isopropylbenzene)

Exp. No.	Isobutyric acid added (mole-%)	O_2 absorbed (in moles after 360 min.)	CO_2 formed (moles per mole O_2)	Exp. No.	Isobutyric acid added (mole-%)	O_2 absorbed (in moles after 360 min.)	CO_2 formed (moles per mole O_2)
1	—	0.078	0.0080	4	3.76	0.272	0.0185
2	1.04	0.364	0.0119	5	7.00	0.348	0.0242
3	1.51	0.337	0.0125	6	27.34	0.344	0.0759

The data of Table 1 show that whereas the addition of 1.04 mole-% isobutyric acid (experiment 2) increases the velocity of autoxidation of isopropylbenzene by a factor of over 4 (compared with the blank experiment), further increase of the quantity of added acid (up to 27.34 mole-%) does not substantially change the amount of oxygen absorbed.

At the same time, an increase of the concentration of isobutyric acid in the mixture leads to a considerable increase in the quantity of carbon dioxide formed. As we see from Table 1 and Fig. 2, an increase in the content of isobutyric acid from 1 to 27 mole-% leads to an increase in the quantity of carbon dioxide by a factor of more than 6 (with substantially unchanged quantity of absorbed oxygen).

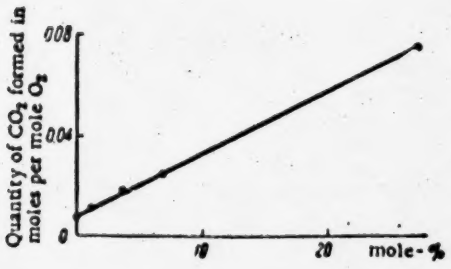


Fig. 2. Dependence of the quantity of carbon dioxide evolved during oxidation of isopropylbenzene in presence of isobutyric acid on the concentration of the latter in the mixture. Temperature 80.5°; initiatorcobalt acetate ($0.9 \cdot 10^{-4}$ mole per mole of isopropylbenzene).

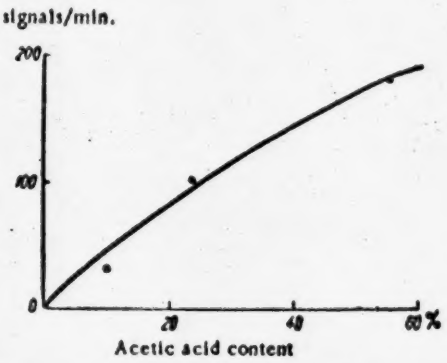
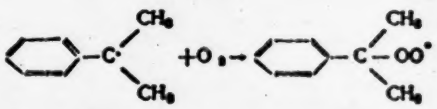


Fig. 3. Change of radioactivity of $BaCO_3$ precipitate as a function of the content of $CH_3C^{14}OOH$ in a mixture with isopropylbenzene. Temperature 80.5°; initiator cobalt acetate ($0.9 \cdot 10^{-4}$ mole per mole of isopropylbenzene).

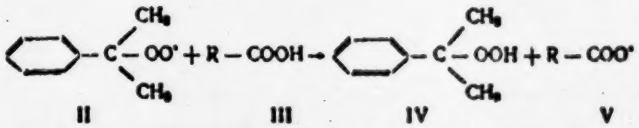
The results of the experiments on oxidation of isopropylbenzene in admixture with radioactive acetic acid (labeled in the carboxyl) confirm that the carbon dioxide originates from the carboxyl group of the acid added (in part at least). Indeed, as evident from Fig. 3 the radioactivity of the precipitated barium carbonate (formed by absorption of CO_2) increases with increasing content of acetic acid in the mixture, the resultant plot being nearly rectilinear. Experiments on the oxidation of acetic, butyric, isobutyric and stearic acids, carried out under similar conditions (80.5°, $0.9 \cdot 10^{-4}$ mole cobalt acetate) but in the absence of isopropylbenzene, showed that neither oxygen absorption nor carbon dioxide formation takes place in the case of acetic and butyric acids. A small amount of carbon dioxide is evolved in experiments on the autoxidation of pure isobutyric and stearic acids; this evidently originates from a process linked to the autoxidation of these acids. The linked decarboxylation of organic acids in course of autoxidation of hydrocarbons may be represented by the following scheme:

1. Formation of a radical of isopropylbenzene hydroperoxide:



I II

2. Interaction of the isopropylbenzene hydroperoxide radical (II) with the organic acid with formation of the acid radical (V):

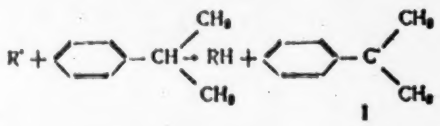


II III IV V

3. Decarboxylation propen

$$\underset{\text{V}}{\text{k} - \text{COO}^{\cdot}} \rightarrow \underset{\text{VI}}{\text{R}^{\cdot}} + \text{CO}_2,$$

4. Detachment of a hydrogen atom from the isopropylbenzene at the tertiary group due to reaction with R' radical formed:

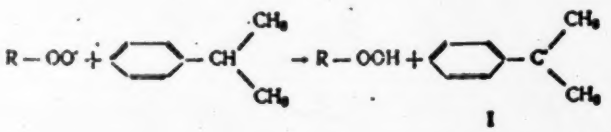


I

This reaction leads to regeneration of the original radical (I) so that the main chain reaction can continue. Account must, of course, also be taken of the possibility of oxidation of the R' radical with formation of the hydroperoxide radical:

$$\text{R}^{\cdot} + \text{O}_2 \rightarrow \text{R} - \text{OO}^{\cdot},$$

which further reacts with a molecule of isopropylbenzene, when the original radicals of (I) are likewise regenerated:



I

According to the above scheme, reactions 2-4 are thus essentially chain transfer reactions and they cannot therefore retard or accelerate the course of the chain process as a whole. In practice, however, small additions of acid increase the velocity of oxidation; but further increase of the amount of added acid does not appreciably influence the velocity of autoxidation.

The absence of a relation between velocity of autoxidation and acid concentration in the region of 1-27 mole-% of the latter provides confirmation of the above scheme. At the same time the increased velocity of autoxidation at small concentrations of acid is evidence that the acid also influences the reaction velocity by other routes.

It has thus been shown that in the autoxidation of mixtures of isopropylbenzene and fatty acids, the oxidation of the hydrocarbon initiates the associated process of decarboxylation of the added acids.

LITERATURED CITED

[1] B. V. Erofeev, N. L. Mitskevich and T. L. Soroko, Bull. Acad. Sci. Belorussian SSR, No. 2, 131 (1955).

[2] N. L. Mitskevich and T. I. Soroko, Trans. Inst. Chem. Acad. Sci. Belorussian SSR, No. 5, 174 (1956).

[3] N. A. Shilov, Linked oxidation reactions, 1905.*

[4] C. D. Hurd, Pyrolysis of carbon compounds, Moscow, 1938, p. 215.*

[5] C. H. Bamford and M. L. S. Dewar, J. Chem. Soc., 1949, 2877.

* In Russian.

[6] I. B. Senderens and I. Aboulenc, Compt. rend. 170, 1064 (1920).

[7] V. V. Korshak and S. V. Rogozhin, Doklady Acad. Sci. USSR, 76, No. 4, 539 (1951).

[8] Yu. V. Karyakin and I. I. Angelov, Pure chemical reagents, 1955, p. 289.*

[9] B. V. Erofeev, A. I. Chirko and L. I. Sorokina, Sci. Memoirs Belorussian State Univ., Chem. Series, part 20, 3 (1954).

Institute of Chemistry of the Academy of Sciences of the Belorussian SSR

Received January 12, 1957

* In Russian.

BLANK
PAGE

SYNTHESIS AND PROPERTIES OF MONO-, DI- AND TRI-p-TOLYLALKYL SILANES

N. S. Nametkin, Academician A. V. Topchiev, Gu Chan-Li and N. A. Leonova

A large number of papers have been published in recent years which describe methods of preparation and properties of silicohydrocarbons of diverse structures. Derivatives of silicohydrocarbons containing functional groups in the organic radical have hitherto been scarcely studied; they are of potential theoretical and practical interest. We were interested in the preparation of silicohydrocarbons containing p-tolyl radicals and in the study of the possibility of utilizing them as intermediates for the synthesis of compounds containing functional groups in the organic radical.

Silicohydrocarbons containing a p-tolyl radical have hardly been investigated. The literature describes tetra-p-tolylsilane [1,2], tri-p-tolylsilane [3], phenyl-p-tolylsilane [4,5] and naphthyl-p-tolylsilanes [6-8]. Of the alkyl-p-tolyl derivatives of silicon, only tri-p-tolylmethylsilane [3], di-p-tolyldimethylsilane [9], p-tolyltrimethylsilane [10,11] and p-tolyltriethylsilane [12] have been described.

In the present communication we describe mono-, di- and tri-p-tolylalkyl derivatives of silicon whose properties are detailed in Tables 1 and 2.

p-Tolyl-chloro(ethoxy)silanes

p-Tolyltrichlorosilane and di-p-tolyldichlorosilane were obtained from silicon tetrachloride and p-tolyl magnesium bromide, and their properties agree with those reported in the literature [13-15].

p-Tolyltriethoxysilane (Table 1), di-p-tolyldiethoxysilane (Table 1) and tri-p-tolylethoxysilane (Table 2) were obtained from tetraethoxysilane and p-tolyl magnesium bromide.

p-Tolyldipropylethoxysilane was isolated from the products of reaction during synthesis of di-p-tolyldipropylsilane (see below and Table 1).

p-Tolyldiisobutylethoxysilane was prepared by reacting isobutyllithium with p-tolyltriethoxysilane. Reactants were 45 g (0.33 mole) isobutyl bromide, 5.3 g (0.8 mole) lithium and 22 g (0.09 mole) p-tolyltriethoxysilane. The reaction mixture was heated 10 hours and gave 9.5 g (yield 38.8%) of p-tolyldiisobutyltriethoxysilane (Table 1).

Mono-, di- and tri-p-tolylalkylsilanes

p-Tolyltrimethylsilane. To p-tolyllithium, prepared from 8.4 g lithium and 94 g p-bromotoluene, was added 54.5 g trimethylchlorosilane, and the mixture was heated 8 hours. Yield 58.2 g (71%).

p-Tolyltriethylsilane. To ethyllithium, prepared from 3.2 g lithium and 21.8 g ethyl bromide, was added 12 g p-tolyltriethoxysilane. The mixture was heated 10 hours. Yield 5.5 g (56.6%).

p-Tolyltripropylsilane. To propyllithium, prepared from 6 g lithium and 44.3 g propyl bromide, was added 23 g p-tolyltrichlorosilane. The mixture was heated 10 hours. Yield 10.8 g (43.2%).

p-Tolyltributylsilane. To p-tolyllithium, prepared from 3.5 g lithium and 34 g p-bromotoluene, was added 38 g tributylethoxysilane, and the mixture was heated 10 hours. Yield 34 g (73%).

p-Tolyltriisoamylsilane. To isoamyllithium, prepared from 6.5 g lithium and 53.8 g isoamyl bromide (1-bromo-3-methylbutane), was added 17.7 g p-tolyltrichlorosilane. The mixture was heated 8 hours and gave 10.7 g (yield 41%).

TABLE 1

Formula of compound	B.p. °C/mm mercury	d_4^{20}	n_D^{20}	MR_D found	MR_D calc.	Found % C	Found % H	Calculated % C	Calculated % H
$CH_3-C_6H_4-Si-(CH_3)_3$	190–193/736	0.8951	1.4898	54.08	54.59	73.26 73.14	9.87 9.76	73.12	9.82
$CH_3-C_6H_4-Si-(C_2H_5)_3$	92–93/3	0.8927	1.4925	68.53	68.47	75.70 75.61	10.73 10.75	75.65	10.74
$CH_3-C_6H_4-Si-(C_3H_7)_3$	121–122/4	0.8784	1.4862	82.68	82.46	77.71 77.86	11.13 11.14	77.35	11.36
$CH_3-C_6H_4-Si-(C_4H_9)_3$	154–156/3	0.8705	1.4822	96.77	96.25	78.20 78.44	12.15 12.31	78.66	11.80
$CH_3-C_6H_4-Si-(i-C_4H_{11})_3$	148–150/2	0.8645	1.4792	110.35	110.14	79.30 79.62	12.09 12.20	79.45	12.11
$(CH_3-C_6H_4-)_2Si-(CH_3)_2$	128–130/2	0.9709	1.5529	79.13	78.88	80.61 80.71	8.47 8.34	79.97	8.38
$(CH_3-C_6H_4-)_2Si-(C_2H_5)_2$	145–147/3	0.9643	1.5503	88.95	88.22	80.52 80.57	9.08 9.14	80.55	9.01
$(CH_3-C_6H_4-)_2Si-(C_3H_7)_2$	179–180/4	0.9582	1.5478	98.43	97.40	81.35 81.35	9.53 9.44	81.11	9.45
$(CH_3-C_6H_4-)_2Si-(C_4H_9)_2$	194–195/3	0.9469	1.5375	107.52	106.66	81.53 81.43	9.91 9.74	81.45	9.94
$(CH_3-C_6H_4-)_2Si-(i-C_4H_9)_2$	174–176/3	0.9433	1.5345	106.67	106.66	80.75 80.56	10.07 10.14	81.45	9.94
$(CH_3-C_6H_4-)_2Si-(i-C_5H_{11})_2$	180–182/2	0.9304	1.5260	117.14	115.92	81.28 81.31	10.04 10.04	81.50	10.03
$CH_3-C_6H_4-Si-(C_6H_5)_2(OC_2H_5)$	96–100/2	0.9139	1.5897	79.18	78.59	72.95 72.85	10.47 10.46	72.00	10.48
$(CH_3-C_6H_4-)Si(i-C_4H_9)_2(OC_2H_5)$	137–138/3	0.9080	1.4802	89.45	87.75	73.31 73.39	10.86 10.85	73.32	10.86
$CH_3-C_6H_4-Si-(OC_2H_5)_3$	115–117/3	0.9832	1.4664	71.71	70.75	61.70 61.77	8.73 8.84	61.45	8.70
$(CH_3-C_6H_4-)_2Si-(OC_2H_5)_2$	150–152/4	1.0148	1.5302	90.94	89.66	72.20 72.22	8.02 8.14	72.01	8.02

Di-p-tolyldimethylsilane. To p-tolyllithium, prepared from 35.4 g lithium and 425 g p-bromotoluene, was added 129 g dimethyldichlorosilane, and the mixture was heated 8 hours. Yield 160 g (67%).

Di-p-tolyldiethylsilane. To p-tolyllithium, prepared from 13 g lithium and 115 g p-bromotoluene, was added 50 g diethyldichlorosilane. The mixture was heated 8 hours. Yield 67 g (78.6%).

Di-p-tolyldipropylsilane. To p-tolyllithium, prepared from 7 g lithium and 70 g p-bromotoluene, was added 34 g dipropyldiethoxysilane. The mixture was heated 8 hours. Yield 16 g (32.7%).

Fractional distillation of the mixture gave also 9 g p-tolyldipropylethoxysilane (yield 21.7%).

Di-p-tolyldibutylsilane. To p-tolyllithium, prepared from 10.5 g lithium and 114 g p-bromotoluene, was added 71.4 g dibutyldibromosilane and the mixture was heated 8 hours. Yield 52 g (71.2%).

Di-p-tolyldiisobutylsilane. To a mixture of p-tolyl magnesium bromide, prepared from 27 g magnesium and 180 g p-bromotoluene, and isobutyl magnesium bromide prepared from 27 g magnesium and 140 g isobutyl bromide, was added 85 g silicon tetrachloride. The mixture was heated 10 hours. Yield 26 g (16%).

Di-p-tolyldiisoamylsilane. To isoamyllithium, prepared from 4 g lithium and 32.5 g isoamyl bromide, was added 20 g di-p-tolyldichlorosilane. The mixture was heated 8 hours. Yield 9.5 g (38%).

Tri-p-tolylmethylsilane. To methyl magnesium iodide, prepared from 15 g magnesium and 56 g methyl iodide, was added 50 g tri-p-tolylethoxysilane. After removal of the ether, the reaction mixture was heated 10 hours at 100°. Yield 18 g (39.5%).

Tri-p-tolylethylsilane. To p-tolyllithium, prepared from 10 g lithium and 102 g p-bromotoluene, was added 32.8 g ethyltrichlorosilane. The mixture was heated 10 hours. Yield 35 g (53%).

TABLE 2

Formula of compound	B.p. °C/mm mercury	M.p. °C	Found %		Calculated %	
			C	H	C	H
$(CH_3-C_6H_4-)_3Si-CH_3$	197—200/4	91.5—92.5	83.55 83.53	7.76 7.71	83.49	7.64
$(CH_3-C_6H_4-)_3Si-C_2H_5$	190—192/2	72	83.29 83.49	8.14 8.18	83.58	7.93
$(CH_3-C_6H_4-)_3Si-C_3H_7$	208—208/4	54.5—55	83.74 83.58	8.34 8.31	83.66	8.19
$(CH_3-C_6H_4-)_3Si-C_4H_9$	214—216/4	47.5—48	83.83 83.83	8.39 8.37	83.74	8.43
$(CH_3-C_6H_4-)_3Si-iC_4H_9$	197—199/3	68—69	83.70 83.64	8.46 8.53	83.74	8.43
$(CH_3-C_6H_4-)_3Si-iC_5H_{11}$	205—207/3	49—50	83.77 83.79	8.88 8.71	83.58	8.00
$(CH_3-C_6H_4-)_3Si-OC_2H_5$	194—195/3	50—50.5	79.52 79.77	7.61 7.52	79.68	7.56

Tri-p-tolylpropylsilane. To propyllithium, prepared from 12 g lithium and 90 g propyl bromide, was added 70 g tri-p-tolylethoxysilane. The mixture was heated 10 hours. Yield 23 g (33.1%).

Tri-p-tolylbutylsilane. To butyllithium, prepared from 4 g lithium and 34 g butyl bromide, was added 25 g tri-p-tolylethoxysilane. The mixture was heated 8 hours. Yield 3 g (50.4%).

Tri-p-tolylisobutylsilane. To p-tolyllithium, prepared from 8.75 g lithium and 85.5 g p-bromotoluene, was added 33 g isobutyltriethoxysilane. After the ether had been driven off, the reaction mixture was heated 10 hours at 100°. Yield 23 g (43%).

Tri-p-tolylisoamylsilane. To isoamyllithium, prepared from 1 g lithium and 6.5 g isoamyl bromide, was added 15 g tri-p-tolylethoxysilane. The mixture was heated 8 hours. Yield 7 g (43.5%).

All of the tri-p-tolylalkylsilanes were recrystallized from ethyl alcohol.

LITERATURE CITED

[1] A. Polis, Ber., 4, 19 (1871); 18, 1443 (1885); 19, 1023 (1886).

[2] E. A. Bassett and D. Ridge, J. Soc. Chem. Ind., 67, 177 (1948).

[3] R. A. Benkeser and F. J. Riel, J. Am. Chem. Soc., 73, 3472 (1951).

[4] M. Malenthal and M. Hellman, et al., J. Am. Chem. Soc., 76, 6392 (1954).

[5] H. Gilman, J. Am. Chem. Soc., 77, 3916 (1955).

[6] A. D. Petrov and V. S. Chugunov, Proc. Acad. Sci. USSR, 73, 323 (1950).

[7] A. D. Petrov and S. I. Sadykh Zade, Proc. Acad. Sci. USSR, 85, 345 (1952).

[8] P. S. Sanin and A. D. Petrov, J. Gen. Chem., 22, 1124 (1952).*

[9] S. B. Speck, J. Org. Chem., 18, 1689 (1953).

[10] H. Gilman and F. J. Marshall, J. Am. Chem. Soc., 71, 2066 (1949).

[11] H. A. Clark, A. F. Gordon, C. W. Young and M. J. Hunter, J. Am. Chem. Soc., 73, 3798 (1951).

* Original Russian pagination. See C. B. Translation.

[12] R. A. Benkeser and H. Landesman, J. Am. Chem. Soc., 76, 904 (1954).

[13] A. Ladenburg, Ber., 7, 387 (1874).

[14] A. Ladenburg, Lieb. Ann., 173, 143 (1874).

[15] A. R. Steele and F. S. Kipping, J. Chem. Soc., 1929, 2545.

L. M. Gubkin Institute of
Petroleum, Moscow

Received March 25, 1957

DEPENDENCE OF THE RELATIVE HEAT RESISTANCE ON COMPOSITION IN THE SYSTEM Cu-Ni-Si

I. I. Novikov and L. I. Dautova

(Presented by Academician A. A. Bochvar, January 24, 1957)

Numerous investigations have been devoted to the correlation of heat resistance with the phase diagram. The main types of heat resistance/composition diagrams have been derived on the basis of investigation of concrete binary systems and individual cuts of multicomponent systems [1-4].

In the investigations of A. A. Bochvar and M. V. Zakharov [2,3,5] an important role in the improvement of heat resistance was attributed not only to the alloying of the main solid solution but also to the structure and properties of the excess phase co-existing with this solution.

In many papers of I. I. Kornilov, emphasis is placed on the specific role of the solid solution: the maximum heat resistance is often associated with a solid solution saturated to the limit [4,6,7].

The accumulated experimental material shows that the character of the dependence of resistant properties on composition undergoes changes under the influence of various factors such as the temperature [2,3,8,9].

The influence of the nature of the co-existing phases on the character of the dependence of heat resistance on the composition is conveniently followed with the help of radial sections of the complex ternary system in which second phases differing in properties and structure border on the main solid solution. As far as we know, this approach to the study of the dependence of heat resistance on composition has not previously been tried.

The system selected for investigation was Cu-Ni-Si in which at 700° the main solid solution on the basis of copper coexists with phases of various nature: the compound Ni_2Si, γ-phase (Cu-Si) and the ternary compound of the σ-phase (Fig. 1) [10].

The relative heat resistance was evaluated by long-term hardness tests [11]. The long-term hardness was measured at 700°; indentations were made with a cone of refractory steel with an angle at the vertex of 90°.

Cu-Ni and Cu-Si binary alloys and the ternary alloys present in six radial cuts were investigated (Fig. 1).

The long-term hardness was determined on specimens cast in a graphite mould without any preliminary heat treatment. This procedure was followed because the silicon-nickel bronzes are of interest as materials for certain cast articles used at high temperatures.

Results of tests are plotted in "long-term hardness/composition" diagrams (Figs. 2 and 3).

Microscopic examination showed that the alloys with maximum long-term hardness sometimes consisted predominantly of one phase and were at other times more or less heterogeneous; in the latter case the second phase was easily visible under medium magnifications.

In Fig. 4 the curves of equal long-term hardness at 700° (isosclercs) are plotted in a triangle of concentration. Here again we show the microscopically established limit of the single-phase region for specimens cast in a graphite mould.

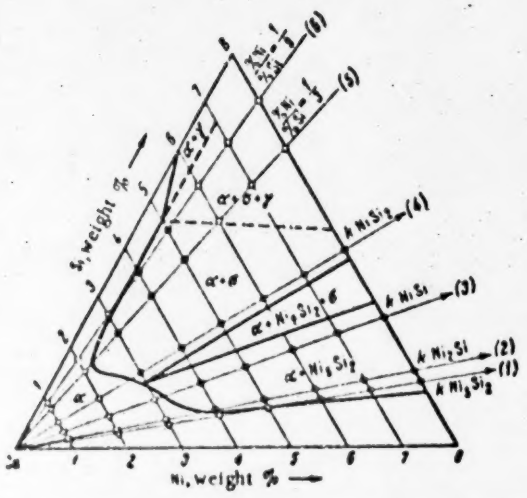


Fig. 1. Isothermal section of the system Cu-Ni-Si at 700° [10]. Numbers in brackets are the serial numbers of the sections.

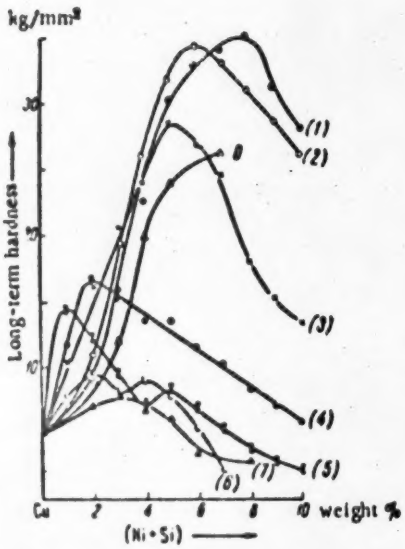


Fig. 2. Long-term hardness at 700° as a function of composition for various cuts of the system Cu-Ni-Si. Numbers in brackets are the serial numbers of the cuts (see Fig. 1); 0) system Cu-Ni; 7) system Cu-Si.

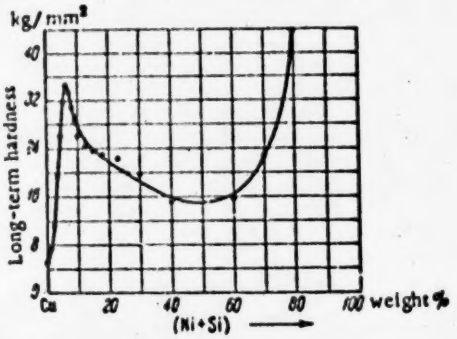


Fig. 3. Long-term hardness at 700° as a function of composition in the Cu-Ni_2Si section.

The different position of the maximum of heat resistance relative to the boundary of the single-phase region may be accounted for if we take into consideration the relative long-term hardnesses of the second phase and of the solution on the basis of copper.

In alloys of the first, second and third cuts, in which the maximum of heat resistance lies in the two-phase region, the second phase is not the compound Ni_2Si (as previously assumed) but the solid solution on

the basis of the silicide Ni_5Si_2 (Fig. 1) [10,12]. The heat-resistant phase Ni_5Si_2, which is distributed along the boundaries of the dendrites, has a blocking effect on the copper solution and increases the heat resistance of the alloy.

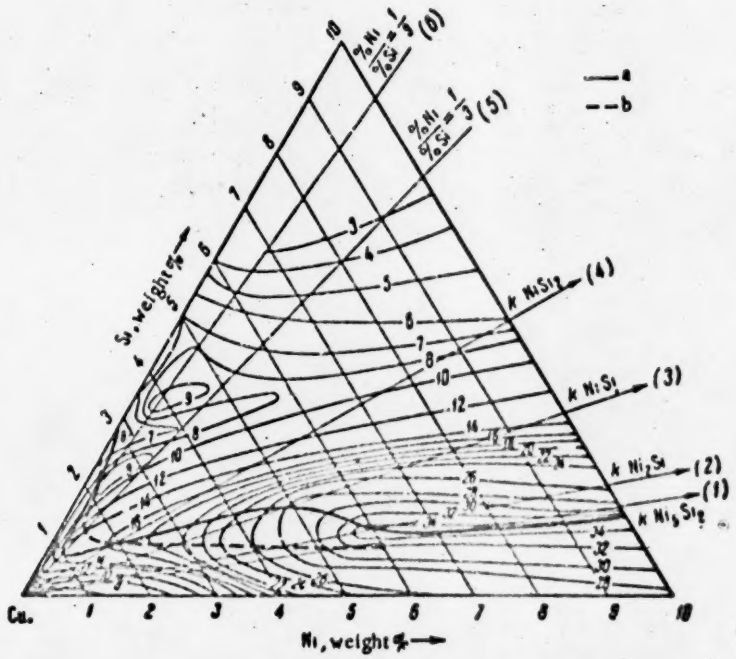


Fig. 4. Curves of equal long-term hardness (isosclores) at 700° in the system Cu-Ni-Si; a) maxima of long-term hardness; b) boundary of the single-phase region.

Excessive heterogenization of alloys of the first, second and third cuts leads to lowering of the heat resistance. This is possibly because, with enlargement of the interphase surface, the effect of the "solution precipitating" mechanism of plasticity [5] is intensified. The solubility of nickel and silicon in copper markedly diminishes with falling temperature [10], while the compound Ni_5Si_2 itself is capable of dissolving a large quantity of copper [12].

A fresh increase in heat resistance is observed with a very high content of Ni_5Si_2 in alloys (Fig. 3). The explanation is that a decisive part in these alloys is played not by the interaction of the two phases but by the great hardness of Ni_5Si_2 which becomes the main alloy.

In the system Cu-Si the maximum heat resistance is manifested by the alloy with the minimum content of γ-phase, since this phase is slightly more heat-resistant than a solution of silicon in copper.

In the fifth and sixth sections, the maximum of heat resistance occurs in the single-phase region of the solid solution. Alloys of these cuts with solid solution on the basis of copper are bordered by a ternary compound (σ-phase) formed by peritectic reaction at 915° [10,12] (Fig. 1). The test temperature of 700° is a high "homologous" temperature for the σ-phase which is evidently not heat-resistant under these conditions. Development of σ-phase in the alloy leads to lowering of the heat resistance.

A slight second rise in the long-term hardness curves of the fifth and sixth cuts is caused by premature development of γ-phase due to non-equilibrium crystallization; this phase is slightly more heat-resistant than σ-phase.

A considerable influence upon the magnitude of the long-term hardness values of the alloys, including alloys with a heat-resistant second phase, is exerted by the alloying of the main solid solution. The relation between heat resistance and alloying of the solid solution on the basis of copper is clearly illustrated by the following comparison. Silicon in the binary system Cu-Si increases the heat resistance of the solid solution less markedly than nickel does in the binary system Cu-Ni (compare curves 0 and 7 in Fig. 2). At the same time, the position of the isosclere in Fig. 4 shows that partial replacement of nickel in the solid solution by silicon (copper content remaining constant) leads to increased heat resistance. This reflects the favorable effect of complex alloying of the solid solution [13].

Consequently, the maximum of heat resistance on the radial cuts of the ternary system is, in general, either in the two-phase (also in the three-phase) region or in the region of the unsaturated solid solution. Coincidence of the maximum of heat resistance with the boundary of the solid solution constitutes a special case. The relative heat-resistant properties of the solid solution (basis of the alloy) and the excess phase have a great influence upon the position of the maximum of heat resistance.

To the three schemes of M. V. Zakharov for the relation between heat resistance and composition [2] must now be added a fourth scheme of great practical importance: the rise of the heat resistance to a maximum located in the heterogeneous region, followed by a fall of heat resistance to a flat minimum, and a fresh rise in heat resistance right up to the composition of the second phase (Fig. 3).

LITERATURE CITED

[1] M. V. Zakharov, Bull. Acad. Sci. USSR, Div. Tech. Sci., No. 1, 124 (1949).

[2] M. V. Zakharov, Proc. Acad. Sci. USSR, 65, No. 3, 337 (1949).

[3] M. V. Zakharov, Investigations on alloys of non-ferrous metals, Collection 1, Acad. Sci. USSR Press, 1955.

[4] L. L. Kornilov, Proc. Acad. Sci. USSR, 96, No. 4, 721 (1952).

[5] A. A. Bochvar, Bull. Acad. Sci. USSR, Div. Tech. Sci. No. 5, 649 (1948).

[6] L. L. Kornilov, Proc. Acad. Sci. USSR, 67, No. 6, 1037 (1949).

[7] L. L. Kornilov, R. S. Mints and S. D. Onoprienko, Proc. Acad. Sci. USSR, 88, No. 4, 683 (1953).

[8] A. A. Bochvar, Bull. Acad. Sci. USSR, Div. Tech. Sci., No. 5, 743 (1946).

[9] L. L. Kornilov and L. I. Pryakhina, Proc. Acad. Sci. USSR, 87, No. 6, 971 (1952).

[10] L. L. Novikov and L. L. Dautova, Coll. Sci. Papers Phys.-Tech. Inst. Acad. Sci. Kazak SSR, 1, 1957.

[11] A. A. Bochvar, Bull. Acad. Sci. USSR, Div. Tech. Sci., No. 10, 1369 (1947).

[12] M. Okamato, Nippon Kinzoku Gakkai Si. 3, No. 9, No. 10, No. 11, 336, 365, 411 (1939).

[13] K. A. Osipov, Proc. Acad. Sci. USSR, 60, No. 6, 1535 (1949).

M. I. Kalinin Institute of Non-Ferrous Metals and Gold, Moscow, and the Institute of Technical Physics of the Academy of Sciences of the Kazak SSR

Received January 23, 1957

PROPERTIES OF α-CELLULOSE DERIVED FROM FOSSIL PINEWOOD OF MILLENIAL AGE

A. I. Skrigan, A. M. Shishko and R. G. Zhbankov

(Presented by Academician B. A. Arbuzov, January 28, 1957)

Production of cellulose and hemicellulose from pine stumps in peat deposits is particularly important for the Belorussian SSR. Examination of cellulose derived from wood of various ages (from one year to 140,000 years) enables us to trace the processes of chemical transformations taking place at comparatively low temperatures in the course of many thousands of years and without any complicating of extraneous factors.

Investigations of the terpenes, resin acids and wood of thousand-year old pine stumps [1] showed that growth is accompanied by processes of hydrogenation and dehydrogenation within the mass of vegetable tissue that resemble the hydrogenation-dehydrogenation catalysis of N. D. Zelinsky [2]. At the same time processes of decarboxylation and detachment of side chains take place. Processes of dehydration and disproportionation of hydrogen lead to formation from the resin acids of the hydrocarbons fichtelite and retene; carbocyclic compounds are formed from the carbonaceous portion of the wood.

The nature of the transformations of α-cellulose in dependence on the age was studied by chemical [3-7] and physical methods, but also in particular by the method of infrared spectroscopy.

The celluloses were extracted by the sulfate process. Isolation of α-cellulose from the specimens of various ages was effected by treatment of bleached and unbleached cellulose with 17.5% NaOH solution.

The content of α-celluloses is least in young celluloses a month to a year old (81-82%); it reaches its maximum in celluloses from 100-500 year old trees, and gradually falls off again with increasing age. Their content is 88% in celluloses of interglacial age, and these celluloses contain the smallest amount of alkali-soluble substances after their treatment with bleaching powder. Thus, the young celluloses are the least homogeneous in composition, and the interglacial celluloses are the most homogeneous.

Results of determination of the elementary composition of dry α-celluloses of various ages, calculated on the ash-free cellulose, are given in Table 1.

TABLE 1

Elementary Composition of α-Celluloses of Various Ages (in %)

Source of the α-cellulose	C	H	O + N
July shoots, 1 month	44,28	6,63	49,09
Year-old shoots	44,38	6,50	49,12
Trunk, 100 years	44,40	6,21	49,39
Root, 500 years	44,54	6,18	49,28
" 1000 years	44,61	6,12	49,27
" 3000 years	44,79	6,01	49,20
Trunk, 140,000 years	45,18	5,81	49,01

It follows from the data of Table 1 that with increasing age of the cellulose, its content of carbon increases slightly and the amount of hydrogen and oxygen decreases.

Infrared transmission spectra of α-celluloses of different ages were obtained with the help of the IKS-11 infrared spectroscope in the 2 to 7 μ region under constant conditions. Specimens were examined in the form of semitransparent films formed by compression (10 tons/cm²) of fibers of α-celluloses [8,9].

The specimens were thoroughly dried in vacuum over P_2O_5 for 5-6 days. In addition, during the plotting of the infrared spectra they were placed in a special air-free cell over P_2O_5. Whenever possible, a supplementary check was made on the 6.07 μ band (deformation vibration of the water molecule). Concordant absorption in this region indicated that the quantity of combined water in the specimens under comparison was the same.

The error in the determination of the absolute coefficient of absorption was 5-10%, and the error in the relative comparison did not exceed 2-3% since unavoidable errors involved in determination of the thickness of the specimens were excluded, as were also errors due to probable differences in non-absorbed light losses of different specimens and to possible variations in their density, etc. All the investigated specimens were prepared under completely identical conditions. In Fig. 1 are plotted the spectra of α-celluloses derived from pinewood. On comparing the values of the coefficient K in the region of approx. 3 μ for α-celluloses of different ages, we see that the number of hydroxyl groups is the highest in the youngest (June) α-cellulose. The number of hydroxyl groups falls with increasing age. The decrease in the proportion of hydroxyls in interglacial α-cellulose is not associated with the development of the double C=C bond since this would have involved an increase of absorption in the 6 μ region, and such an increase was not observed. A strong band at 3333 cm^{-1} is observed in all of the spectra of the α-celluloses, indicating that the majority of the hydroxyl groups in all samples are linked to a hydrogen bond; even in the youngest (June) α-cellulose, nearly all of the hydroxyls are linked to a hydrogen bond.

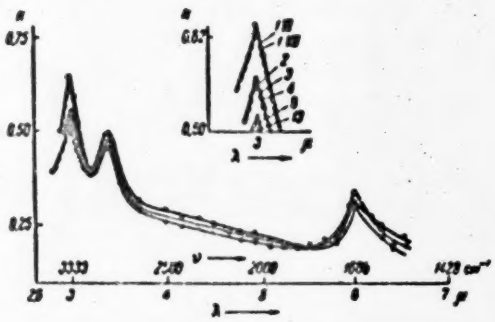


Fig. 1. Spectra of α-celluloses obtained from pinewoods of various ages. 1 V) May; 1 VI) June; 1 VII) July; 2) one year; 3) trunk, 100-years; 4) root, 115 years; 6) root, 1000 years; 8) root, 3000 years; 12) trunk 140,000 years; 13) root, 150,000 years.

Nitrates of α-celluloses were prepared by treatment with HNO_3, density 1.50, in presence of $H_3PO_4 \cdot \frac{1}{2}H_2O$ and P_2O_5 at t = 0° for 6 hours by the Staudinger method as modified by Tsvetaeva and Nikitin [10]. Results of examination of the nitrocelluloses and of determination of the degree of polymerization of the α-celluloses of different ages are presented in Table 2.

Table 2 indicates that the degree of polymerization of α-cellulose falls with increasing age.

Analysis of the spectra of the various nitro-α-celluloses (Fig. 2) confirms that the number of nitro groups is highest in year-old nitro-α-cellulose. The nitro-α-cellulose from a century-old tree contains approximately the same number of nitro groups. There are appreciably fewer nitro groups in interglacial nitro-α-cellulose. The shift of the absorption bands of the OH groups in nitro-α-celluloses from 3333 to 3550 cm^{-1} may be accounted for by the rupture of the hydrogen bonds on nitration of cellulose [11].

TABLE 2

Specimen number	Source of unbleached α-cellulose	Nitrogen, content, %	Degree of substitution, γ	Degree of polymerization
1	May trunk, 1 month	12.74	2.49	1200
2	Trunk, 1 year	12.45	2.40	1200
3	Trunk, 100 years	12.02	2.28	1100
5	Root, 500 years (0.5 m)	12.11	2.29	960
6	Root, 1000 years (1.0 m)	11.98	2.23	920
8	Root, 3000 years (3 m)	11.86	2.22	920
12	Trunk, 140,000 years (sapwood)	11.82	2.20	880
13	Root, 140,000 years (section)	10.26	1.77	660

Acetylation of α-celluloses of fossil trees was conducted in a heterogeneous medium and under mild conditions with a mixture of $(CH_3CO)_2O$ (8.417 d), C_5H_5 (19.41 d) and H_2SO_4 (0.16 d), where d is the weight of α-cellulose. The content of CH_3CO groups in the acetates falls slightly with increasing age of the celluloses.

The spectra of the α-acetylcelluloses are plotted in Fig. 3, which shows α-acetylcelluloses are characterized by a new absorption band for the CO groups in the 1730 cm^{-1} region. A study of this band reveals that most acetyl groups occur in July α-acetylcelluloses, a smaller amount in the 100-year old product and still less in the 1000-year old and the interglacial product.

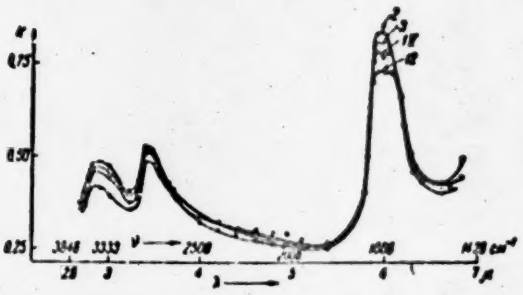


Fig. 2. Spectra of nitro-α-celluloses. See Fig. 1 for key.

Investigation of the exchange reaction of hydrogen with deuterium in the hydroxyl groups of cellulose showed that the hydrogen atoms of not all of the hydroxyl groups enter into reaction [12]. Replacement of hydrogen by deuterium in the hydroxyl groups of different α-celluloses was carried out for 4 hours at 25° (short-period), 116 hours at 55° and 270 hours at 25° (long-term). The spectra of the different α-celluloses deuterated for these various periods are plotted in Fig. 4. Examination of the new band in the 2500 cm^{-1} region, which literature data unequivocally assign to the vibration of the OD groups, shows that both long-term and short-term deuteration give substantially identical results. This is confirmed by the spectrum at the top of Fig. 4 where the broken line relates to the spectrum of preparations which had undergone short-term deuteration and the solid line relates to those which had undergone long-term deuteration. The intensity of the 2500 cm^{-1} band is greatest in June α-cellulose, lower in the 100-year old trunk and rather lower again in interglacial cellulose.

Investigation of the hydrogen bond in the various α-celluloses with the help of the infrared absorption spectra showed that most hydrogen bonds are apparently present in June and interglacial α-cellulose.

In order to determine the content of CH_2 groups in the various α-celluloses, we carried out measurements of absorption in the region of the deformation vibration of the CH_2 groups (1430 cm^{-1}). Inspection revealed a slight tendency towards increase in the content of CH_2 groups with increasing age of α-cellulose.

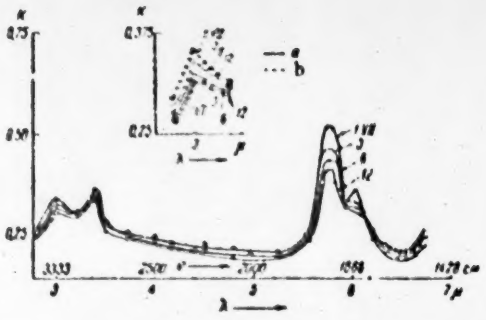


Fig. 3. Spectra of α-acetylcelluloses. a) after acetylation for several days; b) after acetylation for 35 days. See Fig. 1 for key.

Consequently, the α-celluloses originating from pine woods of various ages undergo processes of dehydration and hydrogenation with progressive aging in a similar manner to terpenes and resin acids.

The authors consider it their pleasant duty to express thanks to Professor M. N. Shorygina and to Academician of the Acad. Sci. Belorussian SSR B. L. Stepanov for help in the interpretation of the infrared spectra of the substances investigated.

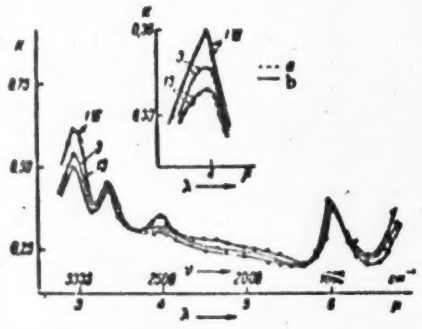


Fig. 4. Spectra of deuterated α-celluloses. a) deuteration for 4 hours; b) deuteration for 270 hours. See Fig. 1 for key.

LITERATURE CITED

[1] A. L. Skrigan, Proc. Acad. Sci. USSR, 80, No. 4, 607 (1951); 90, No. 3, 395 (1953); 100, No. 5, 1135 (1955).

[2] N. D. Zelinsky, Collected Works, 2, 1955, p. 462.

[3] P. P. Shorygin, Chemistry of carbohydrates, Moscow, 1938; Chemistry of cellulose, Moscow, 1939.

[4] Z. A. Rogovin and N. N. Shorygina, Chemistry of cellulose and its associates, Moscow, 1953.

[5] E. D. Kaverzneva, Proc. Acad. Sci. USSR, 78, No. 3, 481 (1951); 68, No. 5, 865 (1949).

[6] V. L. Ivanov, E. D. Kaverzneva and Z. L. Kuznetsova, Proc. Acad. Sci. USSR, 86, No. 2, 301 (1952).

[7] V. A. Kargin and G. L. Slonimsky, Prog. Chem., 24, No. 7, 785 (1955).

[8] R. G. Zhbankov and L. N. Ermolenko, Bull. Acad. Sci. Belorussian SSR, Physics Series, No. 1, 13 (1956).

[9] N. Karlinsky, Chem. Zvesti, 8, No. 7, 452 (1954).

[10] L. P. Tsvetaeva and N. L. Nikitin, Trans. Leningrad Molotov Inst. Tech., part 1 (1949).

[11] V. N. Nikitin, Herald Leningrad State Univ., No. 3, 33 (1950); J. Phys. Chem., 23, 775 (1949).

[12] H. G. Marrinan and L. Mann, J. Appl. Chem., 4, 204 (1954).*

Institute of Chemistry,
Academy of Sciences of the BSSR

Received January 13, 1957

* Original Russian pagination. See C. B. Translation.

ELECTRON PARAMAGNETIC RESONANCE IN SOME CHROMIUM-CONTAINING AROMATIC COMPOUNDS OF SANDWICH STRUCTURE

Yu. D. Tsvetkov, V. V. Voevodsky, G. A. Razuvaev, Yu. V. Sorokin and G. A. Domrachev

(Presented by Academician A. N. Nesmeyanov, April 19, 1957)

Interest has recently increased greatly in the investigation of compounds with a sandwich structure of the type of ferrocene $Fe(C_5H_5)_2$, the ferricene ion $[Fe(C_5H_5)_2]^+$ and analogous molecules with aromatic addends $Cr(C_6H_6)_2$, $[Cr(C_6H_6)_2]^+$, etc. In spite of the large number of publications in this field, there is still no general theory to account for the data on the layer structure of these molecules. The very fact of their formation and stability has not been adequately explained on the basis of the generally accepted concepts of valence. The data obtained up till now indicate that in the majority of compounds of this type the bond between the addends and the complex-forming atoms has a covalent character. This is supported, in particular, by magnetic measurements which indicate that these substances are either diamagnetic or possess a magnetic moment corresponding to one, two or (at the most) three unshared electrons [1], whereas the ionic salts of the same metals possess a considerably higher paramagnetism.

No papers describing the results of investigation of such compounds by the method of electronic paramagnetic resonance (EPR) have hitherto appeared. Such measurements can prove extremely useful for elucidation of certain details of the structure of molecules with sandwich structure.*

The present work is devoted to measurement of the EPR spectrum of the following compounds: $Cr(C_6H_6)_2$ (I), $Cr(C_6H_6\text{-}C_6H_5)_2$ (II), $Cr(C_6H_5\text{-}C_6H_5)_2OC_6H_5$ (III) [2,3]. The static magnetic permeability of these substances corresponds to one unpaired electron [4].

Our measurements were carried out with a superheterodyne EPR apparatus constructed in the Institute of Chemical Physics of the Academy of Sciences of the USSR and working at a frequency of approx. 9000 megahertz. The sensitivity of the set-up in observations of the oscillograph pulses corresponds to $5 \cdot 10^{14}$ molecules of the standard radical of diphenyl-picrylhydrazine (DPPH). The widths and g-factors of the paramagnetic absorption lines were measured with the help of a nuclear emitter. Photographs of spectra of compounds I, II and III in polycrystals are shown in Fig. 1 which also includes the signals emitted by the standard specimen of DPPH. Below are given the g-factors of these substances in relation to DPPH ($g = 2.0036$) from the maximum of the absorption curve together with the corresponding half-widths of the lines.

	I	II	III
g-factor	1.975 ± 0.001	1.987 ± 0.001	1.993 ± 0.007
$\Delta H_{\frac{1}{2}}$ (oerst.)	38 ± 2	28 ± 2	26 ± 2

The absorption curves in Fig. 1 for compounds I and II are markedly asymmetric, due to the anisotropies of the g-factor. On replacing I^- by $(OC_6H_5)^-$, this asymmetry substantially vanishes. It also disappears when these compounds are dissolved in organic solvents and in water. In solutions of compounds I, II and III the half width of the absorption curve is constant and amounts to 17 ± 2 oerst., while the g-factors of all of the compounds have the identical value of 1.984 ± 0.001.

* Lutze [8] has attempted to obtain the electronic paramagnetic resonance spectra of the bicyclopentadienyls of iron, chromium, nickel and magnesium. No paramagnetic resonance pulses, however, were detected at room temperature.

The most significant feature in connection with our understanding of the structure of molecules of chromium-containing aromatic compounds seems to be the ultra fine structure of the absorption curve of compounds II and III in solutions. We failed to detect an ultrafine structure of the curve for compound I. The absorption spectrum of compound III in aqueous solution is shown in Fig. 2. The concentration corresponded to 10^{-2}M. The spectrum comprises at least 7 components with ultrafine structure with a distance between the components of 3.5 ± 0.2 oerst. We also observed a similar ultrafine structure for compound II. A spectrum of this type is developed by interaction of an unpaired electron of a molecule with the magnetic nuclear moments of several hydrogen atoms entering into the composition of the molecule. Since in compounds II and III the hydrogen atoms are exclusively in the aromatic rings, the presence of ultrafine structure signifies that the unpaired electron has a density differing from zero in the aromatic addends of the complex. We surmised that the total width of the absorption curve in a solution of compound I is also governed by the components of the ultrafine structure. In that event, replacement of H by D in the aromatic rings of compound I ought to lead to decrease in the width of the absorption curve [5]. This was checked in special experiments.*

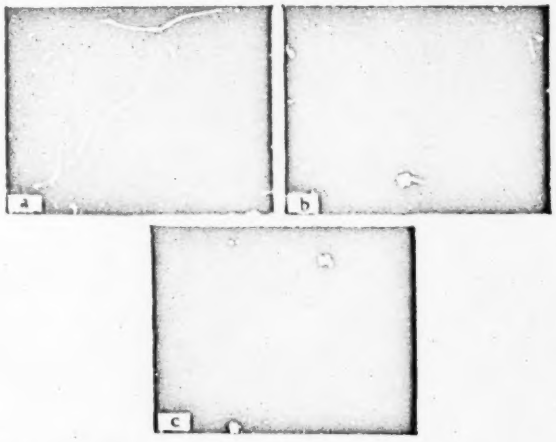


Fig. 1. Paramagnetic resonance spectrum of chromium-containing organic compounds in polycrystals: a) $Cr(C_6H_6)_2I$ (I); b) $Cr(C_6H_5-C_6H_5)_2I$ (II); c) $Cr(C_6H_5-C_6H_5)_2OC_6H_5$ (III). On the left is the signal of the standard (DPPH).

The existence of an ultrafine hydrogen structure of the EPR spectrum may be explained in two ways.

1. The unpaired electron and the positive charge of the complex are localized at the chromium atom. A rough calculation made on this basis shows that the density of the unpaired 3d-electron at the sites of the hydrogen atoms of the aromatic rings is sufficient to give rise to the ultrafine resolution of the EPR spectrum.

2. The unpaired electron and the positive charge are localized in the aromatic addends of the complex. In this event the ultrafine structure is caused by interaction of the unpaired π-electron of the aromatic ring with the hydrogen atoms of this ring. The magnitude of the resolution, the number of components and their relative intensities depend in this event upon the distribution of the electron density round the molecule of addend [6].

The first hypothesis is supported by the following facts: a) The occurrence of anisotropy of the g-factor in compounds I and II; b) the magnitude of the g-factor is lower than that of the g-factor of the free electron (2.0023) [7]. With this hypothesis, however, it is impossible to explain the absence of ultra-fine structure in the case of the dibenzene-chromium ion. Considerable difficulties also arise in this case in attempting to interpret the number of components of the ultrafine structure and their relative intensities.

* The experiments were carried out in our laboratory by V. M. Chibrikin.

Fig. 2. Ultrafine structure of the paramagnetic resonance spectrum of 0.01 M solution of compound III.

If we assume that the unpaired electron is localized at the aromatic addends of the complex, then the number of components and their relative intensities can be satisfactorily accounted for in the case of the bis-diphenyl-chromium ion. The calculation was carried out on the assumption that the electronic density at the H atoms in the para position in bis-diphenyl-chromium is double that at the H atoms in the ortho position and that the hydrogens in the meta position do not participate in the resolution of the levels. The absence of an ultrafine structure on passing to the dibenzene-chromium ion can then be accounted for by the increase in the number of components of the ultrafine structure and, evidently, by a decrease in the distance between the components. With the given homogeneity of the constant of the magnetic field, these factors prevent resolution of the components of the ultrafine structure in the dibenzene-chromium ion.

The true picture of the distribution of the density of the unpaired electron in the investigated compounds evidently involves both of the two limiting cases considered above. A solution to the problem of the precise distribution of the density of the unpaired electron necessitates a quantitative interpretation of the data for the anisotropy of the g-factor in these compounds.

So far, however, the x-ray structural data required for this purpose are not available. The problem can also be attacked by a study of the ultrafine structure of the EPR spectrum of compounds of types I and II with various numbers of different substituents in the rings, as well as of analogous compounds containing the isotope Cr^{53} possessing an inherent nuclear moment which would be capable (in the event of validity of the first hypothesis) of sharply altering the ultrafine structure of the spectrum.

In conclusion the authors express their profound gratitude to Prof. L. A. Blyumenfeld for his help in the evaluation of the results. The authors are also extremely grateful to Prof. B. K. Shembelo, V. M. Chibrikin and Yu. N. Molin for valuable advice and help during the investigation.

LITERATURE CITED

[1] E. O. Fischer, Angew. Chem., 67, No. 17-18, 475 (1955).

[2] G. A. Razuvaev, Yu. A. Sorokin and G. A. Domrachev, Proc. Acad. Sci. USSR, 111, 1264 (1956).*

[3] G. A. Razuvaev, Yu. A. Sorokin, et al., Proc. Acad. Sci. USSR, 113, No. 6 (1957).*

[4] W. Klemm and A. Neuber, Zs. Anorg. Allgem. Chem., 227, 261 (1936).

[5] B. Venkataraman and G. Fraenkel, J. Chem Phys., 24, 737 (1956).

[6] H. McConnell, J. Chem. Phys., 24, 764 (1956).

[7] J. Owen, Disc. Farad. Soc., No. 19, 127 (1955).

[8] E. Lutze, Zs. Phys. Chem., 8, 32 (1956).

Institute of Chemical Physics of the
Academy of Sciences of the USSR
Gorky State University

Received April 13, 1957

* Original Russian pagination. See C. B. Translation.

BLANK
PAGE

CONTRIBUTION TO THE QUESTION OF CONJUGATION IN BUTADIENE

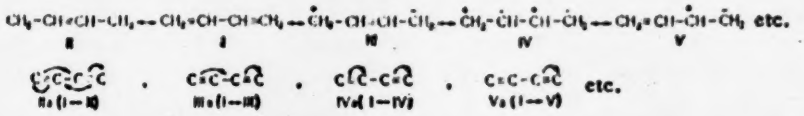
M. I. Batuev

(Presented by Academician I. N. Nazarov, April 25, 1957)

As is well known, the additions of halogens and hydrogen halides to the simplest of the π-conjugated systems, 1,3-butadiene, proceeds as a primary attack in both the 1,2- and 1,4-positions, one or the other predominating depending on the experimental conditions. In the theory of Ingold et al., this dual reactivity has the following explanation [1].

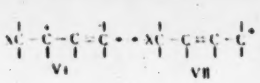
"There are two factors in reactions of π-conjugated systems: the static factor of conjugation (mesomeric effect) and its dynamic factor (electromeric effect)" [2]. The first factor is developed in the unreacting molecule, the second – at the instant of reaction.

The effect of static conjugation is dependent on the predominance in the unreacting butadiene molecule of Structures I and II out of all the structures, I-V and others [3, 4], considered in this theory on the basis of the quantum mechanical description of the molecule by the localized pair method. In another mode of designation, identical in principle [5, 6], the effect is dependent on the predominance of the electron shift IIa (I↔II) [1, 7, 8] out of all possible shifts, IIa-Va and others:

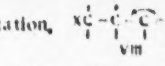


In other terms, the effect of static conjugation (mesomerism) is also characterized in an equivalent manner by the following. In a π-conjugated system, "the p-orbital of the central atom, C_2, overlaps to an equal extent with the p-orbitals of both of the neighboring atoms" [5] (Figure 1). "The π-electron density in all bonds is leveled out to a greater or lesser degree, and the difference between the bonds fades away" [5], to wit: "the usual value for the C–C bond length, 1.54 A, is decreased in butadiene to 1.48 A. The C=C bond length, on the contrary, is somewhat increased" [9]. All of this means that "conjugation of double bonds – a factor which is reflected in the unreacting molecule" [2] – insofar as the observable effect of static conjugation is concerned, lies, perhaps, in a certain mesomeric state of the molecule. In a butadiene molecule in this state, "the 1,4-atoms have a partial free radical character" [4], a centering of the electron density takes place on them [2], a decrease in the covalency of these atoms occurs [1,7,10-12], which also guarantees "increased reactivity of the 1- and 4-atoms" [2], i.e., favorable conditions are created for the attack on these atoms of a positive ion of an electrophylic reagent.

At the instant of an attack the dynamic part of the conjugation effect (the electromeric effect) comes into play – a "summons" [2] for an electron proceeds along the readily polarizable system of conjugated bonds in addition to the electron density already centered (owing to the static part of the conjugation effect) at this atom – the specific importance of electromeric shifts of the type IIIa-Va etc. (structures III-V etc.) is increased. This is culminated in the addition to an atom in the 1- or 4-position of a positive ion X ($X = H^+, Cl^+, Br^+$) with the simultaneous formation, in the terms of Ingold [13] and Baker [11], of a mesomeric carbonium ion, or, in the terms of Wheland [3], of the corresponding resonance hybrid:



VI VII

or, in other notation,  VIII . Just mesomerism of this carbonium ion alone determines the further dual course of the addition reaction, according to the theory under consideration. Ingold wrote [13]: "In reactions of addition to conjugated systems, the intermediate carbonium ion is, of course, mesomeric, having, therefore, two or more positions for neutralization in one molecule in the final stage of the addition" (the 2- and 4-positions in butadiene). In references [2, 14-16], this presence of two neutralization centers is explained in new terms: "inherent center" (in ion VIII, atom 2) and "transfer of the reactive center of the molecule along the system of conjugated bonds" (in ion VIII in atom 4). By the term "transfer of the reactive center" is emphasized the uselessness of the assumption of the separate, independent existence of molecules VI and VII as isomers in the tautomeric process VI ⇌ VII in order to explain the dual reactivity of conjugated systems.* "Dual reactivity is guaranteed by the conjugated system" [2], in 1,3-butadiene by the mesomeric state of one particle, the ion VIII (VI ⇌ VII), by the presence in it of σ,π-conjugation and the delocalization of electrons.

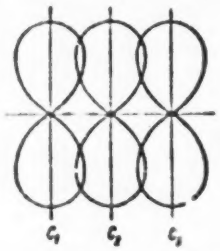


Fig. 1. Overlaping of p-orbitals in a conjugated system of π-bonds.

The theory being considered rests on hypothetical assumptions concerning electron shifts which do not correspond to the facts. Experimental data refute these assumptions.

An undoubted experimental fact is the shortening of the carbon-carbon single bond in butadiene (1.46 ± 0.03 A) in comparison with the carbon-carbon bond in ethane (1.54 ± 0.03 A). This shortening is outside the limits of experimental error. The difference in the results of measurements of the interatomic distance of C=C in butadiene (1.35 ± 0.02 A) and in ethylene (1.353 ± 0.001 A, 1.34 ± 0.02 A, 1.33 A) lies wholly within the limits of experimental error, and according to the available data it is possible to speak of both a lengthening and a shortening of this distance [17]. But data on the vibrational frequencies, which are obtained with enormously greater accuracy than are data on interatomic distances, indicate only a shortening of the C=C interatomic distance in butadiene; the characteristic frequency of C=C in butadiene (1638 cm^{-1}) is substantially higher than in ethylene (1621 cm^{-1}); this increase lies outside the limits of experimental error, and it means that the interatomic C=C distance is less in butadiene than in ethylene [18], i.e., one cannot speak of a mesomeric effect of static conjugation in butadiene of the type IIa (I ⇌ II).

According to this theory, this effect should be still more clearly evident in diacetylene. However, the experimental data indicate the complete absence of it. Actually, the carbon-carbon interatomic distance in diacetylene is sharply decreased, being 1.36 ± 0.03 A as against 1.46 ± 0.03 A in butadiene and 1.54 ± 0.03 A in ethane. But along with this, the C=C distance in diacetylene (1.19 ± 0.03A) as compared to that in acetylene (1.205 ± 0.008 A) not only is not lengthened, but, beyond all doubt, is shortened [17], as is also indicated by the very significant (209 cm^{-1}) increase in the vibrational frequency of the C=C bond in diacetylene (2183 cm^{-1}) in comparison with that in acetylene (1974 cm^{-1}) [19].

The very history of the development of these "dumb-bells" ("figure eights") in the theory of π-conjugated systems is eloquent on the uselessness of the quantum mechanical scheme of Figure 1. The "figure eight" first appeared as a graphical representation of the results of simplified calculations of only one of the members in the well-known expression in polar coordinates for the probability of finding a single valence electron of hydrogen or hydrogen-like atoms in the vicinity of the nucleus in relation to only one polar coordinate – the angle θ ("the latitude"). Specific characteristics of this case are spherical symmetry of the field, a single valence electron, and the absence of the effect of an external field. In the presently considered theory, the thus obtained "figure eight" was transferred to the p-electrons of a carbon atom as the "chief element" and was included in the extremely simplified calculations of complex molecules with multiple bonds, the result of which was, in particular, the quantum mechanical scheme of Figure 1 [4,5,20-22]. This transfer was made in spite of the fact that there is no spherical symmetry of the central field at the carbon of the molecules being considered, there is the effect of the fields of neighboring atoms, and there are four interacting valence electrons.

* "It is more correct to consider as tautomerism only the field of phenomena foreseen by Butlerov – the field of reversible equilibrium isomerization. Then the other field is bounded – the phenomena of dual reactivity and the field of the transfer of the reactive center of a molecule as a result of the phenomenon of resonance and of partial resonance-hyperconjugation coupling" [15].

If the scheme of Figure 1 reflected the real facts, then all of the C=C bonds in butadiene would have to be considered equivalent. However, as we have seen, the interatomic C–C distance in butadiene is close to that of a single bond, and the C=C bonds are shortened. A similar non-equivalency of the C≡C and C–C bonds also occurs in diacetylene (see above).

From the experimental data cited it follows directly that one of the pairs of π-electrons in butadiene is in the possession of the 1,2-carbon atoms, while the other is in the possession of the 3,4-carbon atoms. One of the clearest proofs of this localization of electrons by bonds is the structure of diacetylene; the shortening in it of the C–C distance (1.36 A) to the length of the interatomic distance in the C=C double bond [17] is not accompanied by the appearance of a corresponding characteristic vibrational frequency, since this would require the possession of a second pair of electrons (π-electrons) by the 2,3-atoms, which is actually not the case; the two pairs of π-electrons are strictly localized in the bonds of the 1,2- and 3,4-carbon atoms, guaranteeing full-valued ethylenic bonds (even more shortened and stable).

The mutual interaction of these pairs of π-electrons, which is confirmed by u. v. spectra [23] etc., leads to the two results stated above: 1) a shortening of the single C–C bonds in a π-conjugated system without conversion of the single bond to a double bond;* 2) a shortening of the multiple bonds.

The region in butadiene most enriched with electrons is the region of the 1,4-atoms with methylene, and not methyne, groups, as is indicated by the higher vibrational frequency of methylene groups, particularly in their asymmetric vibrational state [18,26]. It is natural that the positive ion X ($X = H^+, Cl^+, Br^+$) of the reagent is directed to these regions of the molecule; being polarized at the end, they are added to one of the multiple bonds of the system with the formation of the ion $XH_2C-\overset{\uparrow}{C}H-CH=CH_2$. This is the first stage of the reaction, which occurs in due course. The addition of the positive ion proceeds at the expense of equalizing the pair of π-electrons of the interacting pair of π-electrons of the conjugated system. This equalization imparts to the remaining pair of π-electrons a corresponding impulse, reinforcing the strongly increased electronegativity of the C^+ carbon atom, which creates favorable conditions for the transition of IX to X. But the presence in X at the end of the chain of the strongly electronegative C^+ atom in turn, under the appropriate conditions, promotes the transition of X to IX, i.e., a tautomerism between carbonium ions is established:

$$\underset{\text{IX}}{XH_2C-\overset{\uparrow}{C}H-CH=CH_2} \rightleftarrows \underset{\text{X}}{XH_2C-CH=CH-\overset{\uparrow}{C}H_2}$$

This is a case of two tautomeric ions differing in chemical structure (in order of the bonds), and is not a case of a single mesomeric or hybrid ion (IX↔ X). Depending on the conditions of the reaction, the addition of the negative ion (Cl^-, Br^-) can be to ion IX at the 2-position (1,2-reaction) or to ion X at the 4-position (1,4-reaction).

From the above, it is evident that the dual reactivity of butadiene – addition in the 1,2- and 1,4-positions – is explained by the entirely separate existence in space of ions IX and X differing in their chemical structure, and rearranging tautomerically one into the other with the passage of time, and entering into the reaction in its final stage – the addition of a negative ion to butadiene.

LITERATURE CITED

[1] C. Ingold, Structure and Mechanism in Organic Chemistry, Ithaca, N. Y., 1953.

[2] A. N. Nesmeyanov, Sci. Reports Moscow State Univ., No. 132, 5 (1950).

[3] G. Wheland, The Theory of Resonance [and Its Application to Organic Chemistry], Foreign Lit. Press, 1948 (Translation).

* Localization in the 1-2 and 3-4 bonds of the mutually interacting π-electron pairs draws together, as though "from without", the atoms of the C–C bond without the emergence between them of an additional strong interaction brought about by a second pair of electrons (π-electrons), of which there are none in the 2-3 bond and which could only impart to this bond values of parameters characteristic of double bonds. The force constant for the central C–C bond in butadiene and diacetylene is considerably (more than 20%) lower than the force constant for the C–C bond in ethane, as is its vibrational frequency also [24,25].

[14] Ya. K. Syrkin and M. E. Dyatkina, The Chemical Bond and the Structure of Molecules,* Moscow, 1947.

[15] The State of the Theory of Chemical Structure in Organic Chemistry,* Report of the Commission of the Div. Chem. Sci. Acad. Sci. USSR, Izd. AN SSSR, 1954.

[16] M. I. Kabachnik, Prog. Chem., 17, 96 (1948).

[17] C. K. Ingold, Coll. Electronic Theory in Organic Chemistry,* Moscow, 1936.

[18] R. W. Stott, Electronic Theory and Chemical Reactions, London, 1947.

[19] M. V. Volkenshtein, Molecules and Their Structure,* Izd. AN SSR, 1955.

[10] J. Baker, Tautomerism,* Moscow, 1937.

[11] J. Baker, Hyperconjugation, Oxford, 1952.

[12] A. Remick, Electronic Interpretations of Organic Chemistry, Foreign Lit. Press, 1950. (Translation).

[13] P. B. de la Mare, E. D. Hughes and C. K. Ingold, J. Chem. Soc., 1948, 17.

[14] A. N. Nesmeyanov and M. I. Kabachnik, Coll. Questions of Chemical Kinetics, Catalysis, and Reactivity,* Izd. AN SSSR, 1955.

[15] A. N. Nesmeyanov and R. Kh. Freidlina, Jubilee Coll. dedicated to the 30th Anniversary of the Great October Socialistic Revolution,* 1, Izd. AN SSSR, 1947.

[16] O. A. Reutov, Introduction to the book by A. E. Chichibabin, Basic Principles of Organic Chemistry,* 1, Moscow, 1953.

[17] F. Allen and E. Sutton, Acta Crystallogr., 3, 46 (1950).

[18] M. I. Batuev, J. Gen. Chem., 26, 1888 (1956);** Bull. Acad. Sci. USSR, Div. Chem. Sic., 1956, 1329.**

[19] K. Kohlrausch, Raman Spectra, Foreign Lit. Press, 1952 (Translation).

[20] L. Pauling, The Nature of the Chemical Bond [and the Structure of Molecules and Crystals], Moscow, 1947 (Translation).

[21] H. Eyring, J. Walter and G. Kimball, Quantum Chemistry, Foreign Lit. Press, 1948 (Translation).

[22] W. Penney, J. Van Vleck and A. Sherman, The Quantum Theory of Valency,* Moscow, 1938.

[23] Landolt-Börnstein, Zahlen und Funktion, 1, 3, Berlin, 1951.

[24] A. Meister and F. Cleveland, J. Chem. Phys., 15, 349 (1947).

[25] G. Herzberg, Vibrational Spectra of Polyatomic Molecules,* Moscow, 1949.

[26] M. I. Batuev, A. D. Petrov, V. A. Ponomarenko and A. D. Matveev, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1956, 1070; 1956, 1243;** J. Gen. Chem., 26, 2336 (1956).**

Institute of Fossil Fuels
Academy of Sciences USSR

Received March 30, 1957

* In Russian.
** Original Russian pagination. See C. B. Translation.

POLYMORPHISM OF THALLIUM BISULFATE

N. I. Bashilova

(Presented by Academician G. G. Urazov, December 6, 1956)

Thallium bisulfate crystallizes from aqueous solutions of sulfuric acid as tetragonal plates and as prismatic needles [1-5]. In this connection, it has been proposed that the compound is dimorphic [1,2,6]. The existence of two modifications of $TlHSO_4$ was confirmed by us by crystallographic investigation [5].

It appeared necessary to clarify the nature of this polymorphic transformation, and to determine the temperature and the conditions for stable existence of each of the modifications of thallium bisulfate. With this aim, and also with the aim of discovering still unknown phase transformations in the solid state, we investigated $TlHSO_4$ by thermographic analysis.

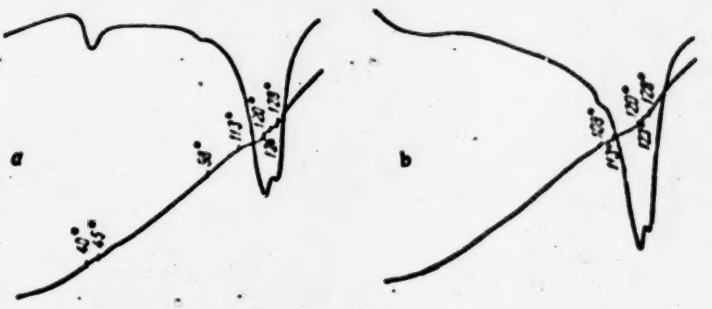


Fig. 1. Heating curve of α-$TlHSO_4$ (a) and β-$TlHSO_4$ (b).

The thermographic analysis was carried out using an N. S. Kurnakov recording pyrometer with a chromel-alumel differential thermocouple. In order to obtain highly reproducible data, such data being required for the comparison of the thermograms of the two [5] modifications of thallium bisulfate, monocrystals [5] of each modification were separately subjected to thermographic investigation. Thermographic recordings of the heating and cooling curves were obtained from monocrystals of $TlHSO_4$ placed in Stepanov cells [7].

Heating curves for the acicular crystals -- α-$TlHSO_4$ -- and for the plates -- β-$TlHSO_4$ -- are presented in Figure 1. A comparison of the differential heating curves shows that they differ by an additional endothermic effect of the α-modification of thallium bisulfate. This effect occurs in the temperature range 40-49°.

The remaining effects on the thermograms are identical. The minimum on the differential heating curve corresponding to the first of these remaining effects is a very small but highly reproducible endothermic effect varying on the individual thermograms in the range 96-108°. A second endothermic effect occurred in the temperature range 113-120°, and a third -- in the range 124-128°.

From the cooling curve and the subsequently obtained heating curve of the fused salt, and also from visual observations of these processes, it can be concluded that the first of the two effects of β-$TlHSO_4$ corresponds to an enantiotropic polymorphic transformation of thallium bisulfate. The last of the effects corresponds to melting of the salt. The low-temperature endothermic effect of the α-modification of thallium bisulfate corresponds to the transition of the α-form of thallium bisulfate to the β-form. This is confirmed by the fact that during heating to 60°, the index of refraction of the acicular crystals of α-$TlHSO_4$ changes without a change in external crystal form, becoming equal to the refractive index of β-$TlHSO_4$ [5] after heating. The reverse transition of the β-modification of thallium bisulfate to the α-modification was not recorded on either the cooling curves or the curves obtained by subsequent heating of the fused salt.

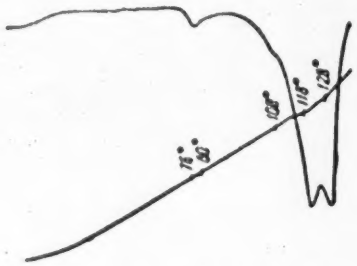


Fig. 2. Heating curve of fused $TlHSO_4$ after slow cooling.

By an investigation of phase transformations under various conditions of cooling of the molten thallium bisulfate, we were able to establish that the reverse transition of β-$TlHSO_4$ to the low-temperature α-modification occurs only with very slow cooling. If the thallium bisulfate crystals are melted and then allowed to cool by shutting down the electric furnace, which has good insulation, then the subsequent heating curves of such fused samples record the low-temperature endothermic effect characteristic of α-$TlHSO_4$ (Figure 2). This indicates that the β-modification converts to the α-modification during slow cooling.

It is characteristic that the temperature of the endothermic effect corresponding to the conversion of the α-form to the β-form of the $TlHSO_4$ for the slowly cooled thallium bisulfate (Figure 2) is higher than that at which this transformation is recorded when directly heating crystals of α-$TlHSO_4$ (Figure 1).

It was established by this investigation that thallium bisulfate has three enantiotropic polymorphic transformations, and that it melts without decomposition. The melting point found for thallium bisulfate is higher than that published in the literature [8,9].

LITERATURE CITED

[1] W. Stortenbeker, Rec. trav. Chim., 21, 91 (1902).

[2] W. Stortenbeker, Rec. trav. Chim., 26, 248 (1907).

[3] D. Ans, Zs. anorg. Chem., 65, 231 (1910).

[4] G. G. Urazov and N. L. Bashilova, Proc. Acad. Sci. USSR, 101, No. 4, 693 (1955).

[5] N. L. Bashilova and M. N. Lyashenko, Proc. Acad. Sci. USSR, 114, No. 2 (1957).*

[6] Gmelins Handbuch anorg. Chem., 38, 361 (1940).

[7] A. V. Nikolaev, L. G. Berg and E. Ya. Rode, Thermography,* Izd. AN SSSR, 1944, p. 58.

[8] W. Stortenbeker, Rec. trav. Chim., 21, 90 (1902).

[9] Handbook of Chemistry,* 2, 1951, p. 213.

Received November 18, 1958

* Original Russian pagination. See C. B. Translation.
** In Russian.

ON THE TWO COURSES OF REACTION IN THE DEHYDROCHLORINATION OF LOWER ALKYLENE CHLOROHYDRINS

P. V. Zimakov and L. M. Kogan

(Presented by Academician B. A. Kazansky, April 1, 1957)

In 1959, a hundred years will have passed since A. Wurtz described the dehydrochlorination of ethylene chlorohydrin in alkaline medium with the formation of a new compound – ethylene oxide [1].

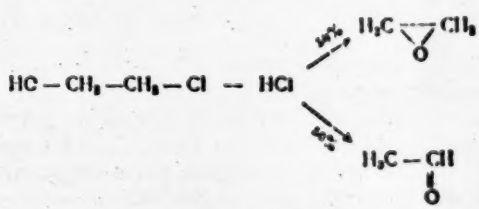
$$Cl-CH_2-CH_2-OH + KOH \rightarrow H_2C\!\!-\!\!CH_2 + KCl + H_2O \quad (O)$$

At present, this reaction forms the basis of the commercial production of ethylene oxide from ethylene and chlorine [2]. In practice, the ethylene oxide always contains approximately 1-2% of acetaldehyde as an impurity when this reaction is carried out with milk of lime (aqueous calcium hydroxide suspension) [3]. Until recently, no significance was attached to this circumstance, or else it was considered probable that the small amount of aldehyde impurity could have been formed by isomerization of the ethylene oxide:

$$H_2C\!\!-\!\!CH_2 \rightarrow H_3C-CH \quad (O)$$

In 1939, a French patent was issued [4] for the production of considerable amounts of aldehydes (or ketones) along with α-oxides by the dehydrochlorination of aliphatic chlorohydrins in a "milk of magnesia" medium. The subject matter of this patent did not call the attention of chemists to the dual reactivity of the simple compound, ethylene chlorohydrin.

Several years ago [5], we undertook a detailed study of the course of the dehydrochlorination of ethylene chlorohydrin (ECH) in various media and under various conditions. We showed that the addition of calcium chloride to the usually used medium of "milk of lime" increases the yield of acetaldehyde during the decomposition of ECH to 3-4%. We also confirmed the course of the dehydrochlorination of ECH in boiling "milk of magnesia." Under the conditions of our experiments, up to 98% of the ECH was dehydrochlorinated; of this, up to 35% formed ethylene oxide, up to 50% formed acetaldehyde, and about 15% of the ECH was converted to ethylene glycol. In special experiments, we showed that the ethylene glycol was formed only by hydration of the first formed ethylene oxide. Taking this last into consideration, it can be said that dehydrochlorination of ECH in boiling milk of magnesia (10%) yields approximately equal amounts of ethylene oxide and acetaldehyde:

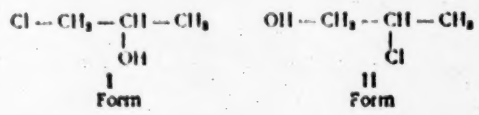


In the course of further observations [5], it was observed that on dehydrochlorination of ECH in a boiling suspension of nickel hydroxide (10% $Ni(OH)_2$) practically the only reaction product formed was acetaldehyde with yields up to 98% based on ECH, and ethylene oxide was present as an "impurity" in insignificant amount.

Thus, it was confirmed that even such a simple compound as ECH has a clearly expressed dual reactivity depending on the reagent acting on it ($Ca(OH)_2$, $Mg(OH)_2$, $Ni(OH)_2$).

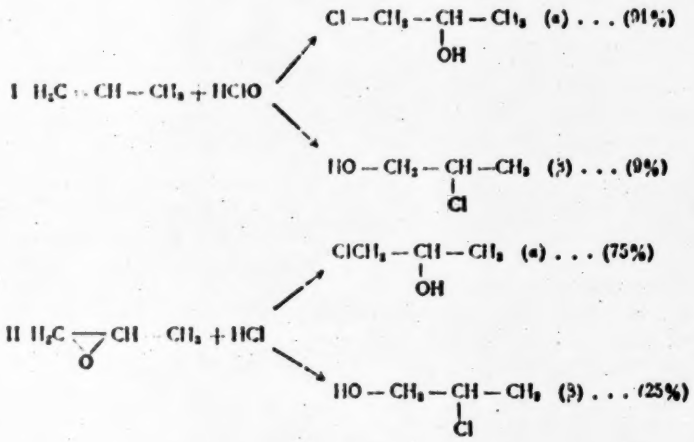
It is of interest to study the reaction peculiarities of the dehydrochlorination of ECH. In this connection, it might first be assumed that, in all of the above cases, the ethylene oxide was the primary product, and the aldehyde was formed from it by isomerization which occurred to a greater or lesser extent (depending on the reagent).

In order to facilitate the problem of experimental confirmation of such an assumption, we turned to the dehydrochlorination of propylene chorohydrin (PCH), taking into consideration that this material exists in two isomeric forms:



The dehydrochlorination of PCH, which proceeds under the same conditions and more easily than ECH, usually does not give propylene oxide yields above 85%. The causes of the decreased yields of propylene oxide from the dehydrochlorination of PCH remain obscure up to the present.

Propylene chlorohydrin can be prepared by two routes, hypochlorination of propylene and hydrochlorination of propylene oxide. We made use of the fact that both of these routes lead to the formation of a mixture of isomers of PCH, the compositions of the mixtures differing appreciably [6].



By decomposition of PCH from either source in boiling "milk of lime" we obtained equal yields of propylene oxide (84-85%). The amount of propionaldehyde was 2-3% of the PCH; more than 10% of the PCH was converted to propylene glycol. We showed that the conversion of PCH into the glycol, just as in the case of ECH, does not proceed by direct saponification of the chlorine, but through the intermediate formation of propylene oxide and its subsequent hydration. The yield of propylene glycol was greater than the yield of ethylene glycol from the dehydrochlorination of ECH, because propylene oxide is more easily hydrated than is ethylene oxide [7]. In complete agreement with this, the yield of propylene oxide from the dehyrochlorination of PCH is less than the corresponding yield of ethylene oxide.

TABLE 1

Dehydrochlorination of Mixtures of Propylene Chlorohydrin Isomers in a Boiling Aqueous Suspension of $Mg(OH)_2$

Isomeric comp of PCH, %		Yield, % of initial PCH					PO + PG / PA + AA
α	β	undecomposed PCH	propylene oxide (PO)	propylene glycol (by diff.) (PG)	allyl alcohol (AA)	propionaldehyde (PA)	
91	9	7.5	62.5	22.2	1.9	5.9	11.2
91	9	7.1	52.0	33.4	1.9	5.6	11.4
91	9	6.5	61.6	24.6	1.7	5.6	11.8
91	9	6.8	60.7	23.0	2.3	6.4	9.7
75	25	1.0*	64.5	9.8	0.3	24.4	3.0
75	25	1.3*	67.2	6.3	0.2	25.0	2.9

* Milk of magnesia strengthened (to 30% $Mg(OH)_2$, and the amount was greater with respect to PCH (500%).

In Table 1 we present the results of the dehydrochlorination of two isomeric mixtures of PCH in excess (to 300% of stoichiometric) boiling "milk of magnesia" (about 15% $Mg(OH)_2$).

The data presented in Table 1 provide us with a basis for forming a conclusion with respect to the dependence of product distribution on the isomeric composition of the original PCH.

Thus, with a change in this composition from $\frac{\alpha}{\beta} = 10:1$ to $\frac{\alpha}{\beta} = 3:1$, the ratio of products formed varies similarly, as may be seen from the last column of the table. It is evident that the aldehyde and alcohol are formed only from the β-isomer, or at least principally from it. We then turned to experiments on the dehydrochlorination of mixtures of isomers of PCH in a boiling suspension of nickel hydroxide. As was stated above, in such medium ($Ni(OH)_2$) ECH is dehydrochlorinated almost wholly with the formation of acetaldehyde. A 20% suspension of $Ni(OH)_2$ with an excess of 200% of stoichiometric was used in the experiments.

The data, presented in Table 2, support to an even greater extent the proposition that propionaldehyde is formed only from the β-isomer of PCH. This becomes still more evident if the yield of propionaldehyde is calculated only on the β-isomer; it then averages about 85%.

TABLE 2

Dehydrochlorination of Isomeric Mixtures of Propylene Chlorohydrin in a Boiling Aqueous Suspension of $Ni(OH)_2$

Isomeric composition of PCH, %		Yield, % of initial PCH				
α	β	undecomposed PCH	propylene oxide	propylene glycol	propionaldehyde	allyl alcohol
75	25	69.2	4.2	4.8	21.3	0.4
75	25	69.8	3.6	4.3	21.6	0.4
75	25	71.8	4.6	5.0	18.3	0.5

We isolated the unreacted PCH from the reaction mixture (Table 2). Obviously, it should consist entirely of the α-isomer, since the β-isomer was dehydrochlorinated in the $Ni(OH)_2$ medium.

Using this PCH (α-isomer), we repeated the dehydrochlorination experiment under the former conditions, i.e., an excess of a boiling aqueous suspension of $Ni(OH)_2$. As would be expected, there was absolutely no reaction; appreciable amounts of dehydrochlorination products were not observed. We carried out a parallel dehydrochlorination of another portion of this same PCH, but using a boiling aqueous suspension of $Ca(OH)_2$; in this case, a high yield of propylene oxide (about 85%) was obtained.

SUMMARY

1. Propionaldehyde is formed in considerable amounts during the dehydrochlorination of PCH only in suitable media such as an aqueous suspension of magnesium hydroxide and, especially, nickel hydroxide. In this respect, the same rule applies as in the dehydrochlorination of ECH.

2. Propionaldehyde is formed during dehydrochlorination of PCH in an appropriate medium ($Ni(OH)_2$) only from the β-isomer. The α-isomer not only does not form the aldehyde under these conditions, but generally is not dehydrochlorinated.

3. The α-isomer of PCH, just as the β-isomer, dehydrochlorinated with equal ease in basic media (NaOH, KOH, $Ca(OH)_2$) with the formation of propylene oxide. The formation of propionaldehyde during dehydrochlorination of PCH is not due to isomerization of propylene oxide.

4. During dehydrochlorination of ECH with $Mg(OH)_2$ and $Ni(OH)_2$, acetaldehyde is formed not as a result of isomerization of ethylene oxide, but directly from the ECH by an independent process.

5. Such simple compounds as ECH and PCH develope a dual reactivity during dehydrochlorination, the course of the reaction depending on the medium in which the dehydrochlorination is carried out; in one case splitting out a molecule of hydrogen chloride yields an α-oxide, in the other case it yields carbonyl compounds (aldehydes).

LITERATURE CITED

[1] A. Wurtz, Lieb. Ann., 110, 125 (1859); Ann. Chim. Phys., 55, 400 (1859).

[2] P. V. Zimakov, Ethylene Oxide,* Moscow, 1946.

[3] L. M. Kogan, Production and Processing of Ethylene Oxide in Germany,* Moscow, 1947.

[4] French Patent, 850,752, 1939, Chem. Abstr., 1950, 2 (1942).

[5] L. M. Kogan, A Study of the Chemical and Technological Characteristics of the Production of Ethylene Oxide and Acetaldehyde from Ethylene Chlorohydrin, Dissertation, Moscow, 1951.

[6] L. Smith and S. Skule, Acta Chem. Scand., 4, 39 (1950).

[7] A. Eltekov, J. Russ. Phys.-Chem. Soc., 14, 355 (1882).

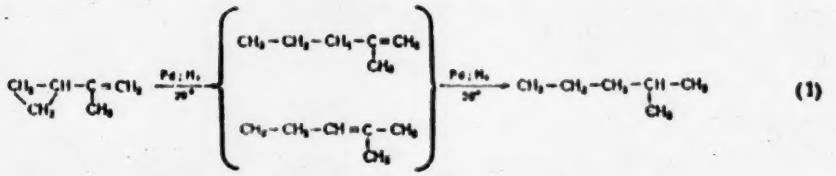
Received March 28, 1957

*In Russian.

HYDROGENATION OF VINYLCYCLOPROPANE AND 1-METHYL-1-ISOHEXENYLCYCLOPROPANE IN THE PRESENCE OF PLATINUM AND PALLADIUM

Academician B. A. Kazansky, M. Yu. Lukina and L. G. Salnikova

It was recently found [1] that in the presence of palladium black at room temperature isopropenylcyclopropane readily adds two moles of hydrogen with the formation of 2-methylpentane. It was shown that the reaction proceeds through the intermediate formation of 2-methyl-1-pentene and 2-methyl-2-pentene according to the reaction:

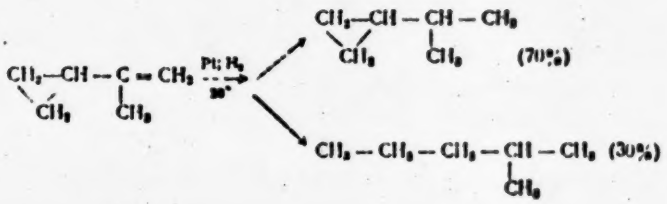


(1)

To all intents and purposes, isopropylcyclopropane is not formed under these conditions.

This rather singular behavior of isopropenylcyclopropane forces us to assume that the double bond present in the side chain of this compound reduces the stability of that C–C bond of the three-membered ring which is next to the substituent, this instability toward splitting with the addition of hydrogen apparently being due to an unusual conjugation between the cyclopropane ring and the double bond.

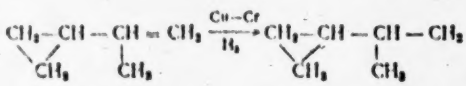
Hydrogenation of isopropenylcyclopropane in the presence of platinum black [2] proceeds differently; 1.3 moles of hydrogen are added, and a mixture consisting of 70% isopropylcyclopropane and 30% 2-methylpentane is obtained:



(2)

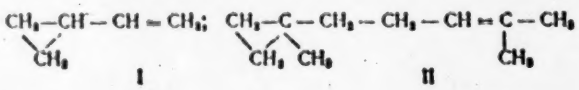
Thus, in the presence of platinum black, splitting of the three-membered ring with the addition of hydrogen, in accordance with the reaction given for palladium (1), proceeds more slowly than the addition of hydrogen across the double bond with retention of the cyclopropane ring. In the first reaction 0.6 mole of hydrogen is consumed, while in the second 0.7 mole is consumed. It is known from the literature [3] that in the presence of copper-chromium catalyst at comparatively high temperatures and under elevated hydrogen pressure, one molecule

of hydrogen can be selectively added to isopropenylcyclopropane with the formation of isopropylcyclopropane:



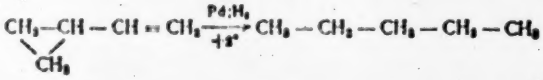
(3)

It should be noted that with both palladium and platinum black there is absolutely no addition of hydrogen to isopropylcyclopropane at room temperature. In the present work, we studied the addition of hydrogen, in the presence of platinum and palladium blacks, to two other hydrocarbons of the cyclopropane series in which there is a double bond in the side chain: vinylcyclopropane (I), in which the double bond is conjugated with the three-membered ring, and 1-methyl-1-isohexenylcyclopropane (II), in which the double bond is separated from the ring by two methylene groups.



I II

In the presence of palladium black, vinylcyclopropane readily (+2°) adds two moles of hydrogen converting to n-pentane; i.e., in this case, cleavage of the three-membered ring with the addition of hydrogen and hydrogenation of the double bond of the side chain occur readily, as was previously observed for isopropenylcyclopropane [1]:

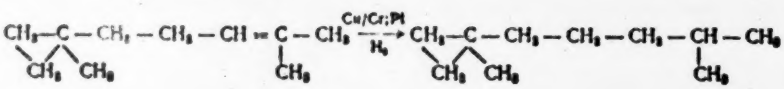


(4)

If the hydrogenation is interrupted with the addition of only one molecule of hydrogen, a more complex mixture is formed; this mixture still has not been studied in detail, but, judging from the distillation curve and the physical properties of the fractions, it contained unreacted vinylcyclopropane, n-pentane, 1-pentene, and 2-pentene.

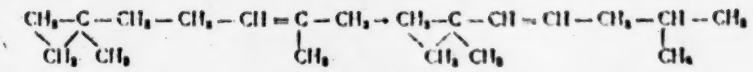
As in the case of isopropenylcyclopropane [2], in the presence of platinum black vinylcyclopropane adds about 1.3 moles of hydrogen, forming a mixture of ethylcyclopropane and n-pentane.

Both in the presence of platinum black at room temperature and in the presence of copper-chromium catalyst at 100° and a pressure of 130 atm., 1-methyl-1-isohexenylcyclopropane is converted to 1-methyl-1-isohexylcyclopropane, a compound previously undescribed in the literature.



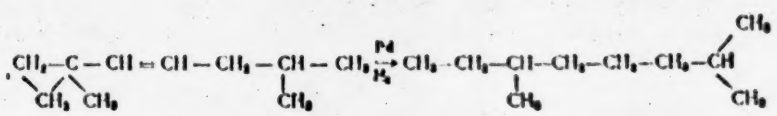
(5)

In the presence of palladium black at room temperature, 1-methyl-1-isohexenylcyclopropane absorbs about 1.6 moles of hydrogen and is converted to a mixture of 1-methyl-1-isohexylcyclopropane and 2,6-dimethyloctane, according to the properties of the hydrogenation product. This result can be explained as follows: a part of the added hydrogen is used in the hydrogenation of the double bond in the side chain according to Equation (5); the other part is added to the isomeric hydrocarbon in which the double bond, under the influence of the palladium black, is shifted to a position of conjugation with the cyclopropane ring.



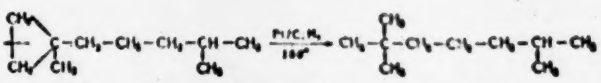
(6)

A similar double bond shift in the presence of palladium was previously observed [1] for 2-methyl-1-pentene, from which was obtained a mixture of 2-methyl-1-pentene and 2-methyl-2-pentene. The 1-methyl-1-isohexenylcyclopropane with the double bond conjugated with the cyclopropane ring, which is formed by isomerization, evidently behaves similarly to vinylcyclopropane and isopropenylcyclopropane in the presence of palladium and hydrogen; i.e., it adds two molecules of hydrogen and is converted to 2,6-dimethyloctane.



(7)

The double bond shift does not proceed in the presence of platinum black, and, therefore, hydrogenation leads only to 1-methyl-1-isohexylcyclopropane. In the vapor phase at 180° and in the presence of platinized carbon, 1-methyl-1-isohexylcyclopropane adds hydrogen and is converted to 2,2,6-trimethylheptane; i.e., in this case, just as with other alkylcyclopropanes [4,5], hydrogenolysis of the three-membered ring proceeds with rupture of the C–C bond across from the substituent.



(8)

EXPERIMENTAL

The vinylcyclopropane was synthesized by the method of Slabey [6], and had the following properties: b.p., 40-40.2°/760 mm; n_D^{20} 1.4140; d_4^{20} 0.7197.

The 1-methyl-1-isohexenylcyclopropane was prepared by the method of Kizhner [7], and had the following properties: b.p. 161-161.5°/760 mm; n_D^{20} 1.4400; d_4^{20} 0.7770.

TABLE 1

Hydrocarbon	B.p. °C (760 mm)	n_D^{20}	d_4^{20}	Aniline point, °C
Ethylcyclopropane [8]	35.94	1.3788	0.6839	—
n-Pentane [9]	36.0	1.3575	0.6262	—
2-Methylbutane [9]	27.85	1.3537	0.6196	—
1-Methyl-1-isohexyl-cyclopropane *	155.1	1.4193	0.7544	57.2
2,6-Dimethyloctane [9]	158.54	1.4113	0.7285	78.1 (crit.)
2,2,6-Trimethylheptane [9]	148.2	1.4050	0.7195	81 (crit.)

* Prepared by us by hydrogenation of 1-methyl-1-isohexenylcyclopropane in the presence of copper-chromium catalyst.

In Table 1 are presented the properties of the hydrocarbons which would be obtained by the catalytic addition of hydrogen to these two hydrocarbons assuming that the hydrogenation proceeded in all possible directions. The methods of hydrogenation and of isolation of reaction products were the same as in our previous work [1]. The palladium and platinum blacks were prepared according to the method of Zelinsky [10].

1. Hydrogenation of vinylcyclopropane. 7.2 g of hydrocarbon, in the presence of palladium black, added hydrogen equivalent to 2 moles per mole. The product was distilled in a column of 40 theoretical plates. The properties of the fractions are presented in Table 2. The distillation data show that the hydrogenation gave almost pure n-pentane, probably with some admixture of unconverted vinylcyclopropane.

In the presence of platinum black, 7.2 g of vinylcyclopropane added hydrogen equivalent to 1.29 moles per mole. Distillation in the same column gave a product having these properties: b.p. 35.6-35.9°/760 mm; n_D^{20} 1.3738; d_4^{20} 0.6723. A comparison of the constants of the catalyzate with the data in Table 1 shows that it was a mixture of ethylcyclopropane and n-pentane, separation of which by distillation is not possible.

TABLE 2

Fraction No.	B.p., °C (760 mm)	Weight, g	n_D^{20}	d_4^{20}
1	36.0—36.1	0.6	1.3585	0.6285
2	36.1—36.2	2.2	1.3578	0.6270
3	36.2—36.3	1.3	1.3576	0.6270
Residue after distillation from Favorsky flask	36.3—36.4	1.3	1.3581	0.6275
Loss	—	0.7	—	—

2. Hydrogenation of 1-methyl-1-isohexenylcyclopropane. 19.0 g of hydrocarbon, in the presence of platinum black, added hydrogen equivalent to one mole per mole. The reaction product distilled, in a column of 40 theoretical plates, at 154.8-155.0°/760 mm; n_D^{20} 1.4193; d_4^{20} 0.7544; i.e., it was pure 1-methyl-1-isohexylcyclopropane (see Table 1).

TABLE 3

Fraction No.	B.p., °C (760 mm)	Weight, g	n_D^{20}	d_4^{20}	Aniline point, °C
1	154.5—154.8	0.4	1.4178	0.7517	—
2	154.8—155.3	1.3	1.4166	0.7493	59.2
3	155.3	7.0	1.4165	0.7488	63.9
4	155.3—155.6	2.2	1.4150	0.7438	65.2
5	155.6—156.0	2.5	1.4143	0.7401	67.1
Loss	—	1.3	—	—	—

15.5 g 1-methyl-1-isohexenylcyclopropane was hydrogenated in the presence of palladium black. Hydrogen was added in an amount equivalent to 1.63 moles per mole. After separation, the reaction product was distilled in a column. The distillation results are presented in Table 3.

Comparing the data of Tables 1 and 3, it can be concluded that the catalyzate consisted of a mixture of 1-methyl-1-isohexylcyclopropane and 2,6-dimethyloctane.

4.5 g of 1-methyl-1-isohexylcyclopropane was passed in a stream of hydrogen at a temperature of up to 180° and a space rate of 0.2 $hour^{-1}$ through a tube containing platinized carbon. The catalyzate was distilled from a Favorsky flask and had the following properties: b.p. 147.6°/760 mm; n_D^{20} 1.4059; d_4^{20} 0.7191. Judging from these data, the hydrocarbon obtained was 2,2,6-trimethylheptane.

LITERATURE CITED

[1] B. A. Kazansky, M. Yu. Lukina et al., Bull. Acad. Sci. USSR, Div. Chem. Sci., 1956, 36.*

[2] B. A. Kazansky, M. Yu. Lukina et al., Bull. Acad. Sci. USSR, Div. Chem. Sci., 1956, 1102.*

[3] V. A. Slabey and P. H. Wise, J. Am. Chem. Soc., 74, 1473, 3887 (1952).

[4] M. Yu. Lukina, V. A. Ovodova and B. A. Kazansky, Proc. Acad. Sci. USSR, 97, 683 (1954).

[5] B. A. Kazansky, M. Yu. Lukina and A. I. Malyshev, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1956, 1399.*

[6] V. A. Slabey, J. Am. Chem. Soc., 74, 4930 (1952).

[7] N. M. Kizhner, J. Russ. Chem. Soc., 50, 1 (1918).

[8] R. V. Volkenburgh, K. W. Greenlee, J. M. Derfer and C. E. Boord, J. Am. Chem. Soc., 71, 172 (1949).

[9] F. D. Rossini, et al., Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds, Pittsburgh, 1953.

[10] N. D. Zelinsky, Selected Works, Izd. AN SSSR, 2, 1941, 150.

Received May 2, 1957

* Original Russian pagination See C. B. Translation.

BLANK
PAGE

ALKYL ESTERS OF ETHYLTHIOARSINOUS [ETHYLTHIOLARSONOUS] ACID

Gilm Kamai and N. A. Chadaeva

(Presented by Academician A. E. Arbuzov, April 13, 1957)

Esters of thioarsenous and alkyl and arylthioarsinous acids have been little studied [1]. Certain esters of arylthioarsinous [arylthiolarsonous] acids have been described in the patent literature as substances possessing therapeutic activity [2].

The synthesis and properties of alkyl esters of ethylthioarsinous acid of the general formula $C_2H_5As(SR)_2$ are described in the present work.

In our investigations we dwelled first on a study of the direct reaction of ethyldichloroarsine with the appropriate mercaptans according to:

$$C_2H_5AsCl_2 + 2RSH \rightarrow C_2H_5As(SR)_2 + 2HCl$$

Experiments on this first method of preparation were carried out as follows. The required amount of mercaptan was placed in an Arbuzov distillation flask, and the ethyldichloroarsine was added to it dropwise from a dropping funnel. The addition of the ethyldichloroarsine was accompanied by vigorous evolution of hydrogen chloride, which was displaced by a current of dry carbon dioxide. After the addition of the ethyldichloroarsine had been completed, the mixture was slowly heated, first to the boiling point of the mercaptan, and then gradually to a temperature of 190-200° over the course of 3 hours. The reaction products were then distilled under vacuum. The ethyl, n-propyl, n-butyl, and isoamyl esters of ethylthioarsinous acid were synthesized by this route.

The ethyl, n-butyl, and n-hexyl esters of ethylthioarsinous acid were prepared by a second method, the reaction of ethyldichloroarsine with the appropriate mercaptan in ether medium and in the presence of anhydrous pyridine.

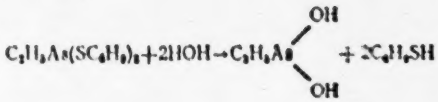
It should be mentioned that the purest preparations were obtained when, after separation of the major part of the pyridine hydrochloride, the filtrate was quickly washed with ice water.

The ethyl ester of ethylthioarsinous acid was also prepared by a third method according to the scheme:

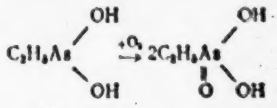
$$2C_2H_5SNa + C_2H_5AsCl_2 \rightarrow C_2H_5As(SC_2H_5)_2 + 2NaCl$$

The constants of the thioesters prepared by us are presented in Table 1. The alkyl esters of ethylthioarsinous acid synthesized by us were colorless, transparent liquids with a disagreeable, penetrating odor, readily soluble in many organic solvents.

Hydrolysis of the alkyl esters of ethylthioarsinous acid in the cold or at ordinary temperatures takes place comparatively slowly; on standing in air, a white precipitate is formed. We obtained ethylarsinic [ethylarsonic] acid on heating the n-butyl ester of ethylthioarsinous acid with water. The formation of this acid can be explained by the following reactions:



(1)



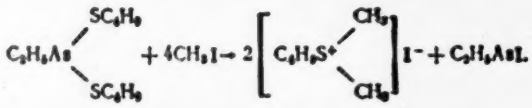
(2)

Equation (1) is identical with the equation for hydrolysis given by Waters and Williams [3] for analogous compounds.

TABLE 1

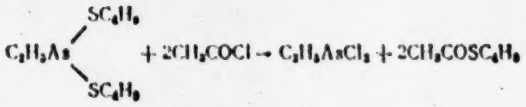
Formula	Prep. method	B.p., °C/mm	d_4^{20}	n_D^{20}	MR_D found	R_D As	As, % found	As, % calc.	S, % found	S, % calc.	Yield %
$C_2H_5As(SC_6H_5)_2$	I	80—82/2	1.2555	1.5750	59.54	10.412	33.51	33.11	28.65	28.35	30.4
	II	81—82/2	1.2593	1.5747	59.34	10.21	32.93	33.11	28.65	28.35	35.5
	III	75—77/1.5	—	1.5749	—	—	33.28	33.11	28.9	28.35	41.9
$C_2H_5As(SC_7H_7)_2$	I	101—102/2	1.1906	1.5565	68.70	10.34	29.38	29.45	25.58	25.22	40.3
$C_2H_5As(SC_6H_5)_2$	I	122—123/2	1.1402	1.5442	78.19	10.69	26.61	26.53	23.26	22.71	54.7
	II	122—123/2	1.1374	1.5441	78.37	10.97	26.12	26.53	22.96	22.71	59.4
	IIa	120—123/2	1.1396	1.5442	78.23	10.63	26.38	26.53	22.51	22.71	43.5
$C_2H_5As(SC_8H_{17})_2$		135—136/2	1.0957	1.5324	87.83	10.99	24.07	24.14	20.99	20.66	43.2
$C_2H_5As(SC_9H_{19})_2$	I	163—164/1.5	1.0778	1.5250	96.62	10.55	21.84	22.13	18.78	18.95	31.3
	II										

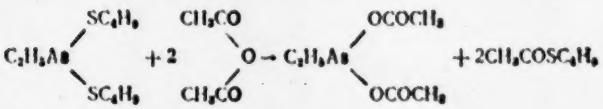
We also studied the reaction of the n-butyl ester of ethylthioarsinous acid with methyl iodide. After an equimolar mixture of methyl iodide and the n-butyl ester of ethylthioarsinous acid had stood for 13 days at a temperature of 20-22°, the resulting white crystals were separated. They melted at 78-80°. They dissolved readily in water and alcohol, and were insoluble in ether. According to the analytical data, this material was dimethyl-n-butylsulfonium iodide. The formation of this compound can be explained as follows:



Thus, it was shown that alkyl esters of ethylthioarsinous acid do not form arsonium type compounds under the influence of methyl iodide, and that in view of the more reactive centers around the sulfur atom, the As–S bond is broken with the formation of sulfonium compounds.

We also studied the reaction of the n-butyl ester of ethylthioarsinous acid with acetyl chloride and acetic anhydride. In both cases, there was a double decomposition reaction similar to the previously studied reactions of acyl chlorides and of anhydrides of carboxylic acids with esters of arsenous and alkylarsinous acids [4] according to:





Both reactions require a heating time of 5 to 18 hours at a temperature of 150-160°. The S-butyl ester of thioacetic [thiolacetic] acid obtained from these reactions was a colorless, transparent liquid with a sharp odor somewhat reminiscent of the odor of butyl acetate. The ester was readily soluble in organic solvents, and immiscible with water. B.p. 89°/74 mm; d_4^{20} 0.9441; n_D^{20} 1.4598.

LITERATURE CITED

[1] M. P. Classon, Bull. Soc. Chim. (2) 25, 185 (1876); R. Klement and R. Reuber, Ber., 68, 1761 (1935); W. A. Waters and J. H. Williams, J. Chem. Soc., (1950), 18; H. J. Bielig, G. Lutzel and A. Reidies, Ber., 89, 3, 775 (1956).

[2] E. Urbschat, USA Pat., 2644005, June 30, 1953; Chem. Abstr., 48, 5879e (1954); S. Matsui and M. Sato, Japan, 24 (51); Chem. Abstr., 47, 3343e (1953); E. A. H. Friedheim, Brit. Pat., 655435, July 18, 1951; Chem. Abstr., 47, 144 (1953); L. A. Sweet and E. W. Tillitson, USA Pat. 2566382 (1951); Chem. Abstr., 2576 (1952); Takahashi and Ueda, U. S. Patent 2,701,812, February 8 , 1955; Ref. J. Chem., No. 4, 10777 P, 1956.

[3] W. A. Waters and J. H. Williams, J. Chem. Soc., (1950), 18.

[4] Gilm Kamai and N. A. Chadaeva, J. Gen. Chem., 26, 2468 (1956)*; Gilm Kamai and N. A. Chadaeva, Proc. Acad. Sci. USSR, 95, 81 (1954); Gilm Kamai and Z. L. Khisamova, J. Gen. Chem., 26, 411 (1956).*

Received April 8, 1957

* Original Russian pagination. See C. B. Translation.

BLANK
PAGE

ON THE FORMATION OF POLYMERIC HYDROCARBONS BY THE DECOMPOSITION OF ALIPHATIC DIAZO COMPOUNDS

Associate Member Acad. Sci. USSR V. V. Korshak and V. A. Sergeev

The decomposition of aliphatic diazo compounds in the presence of various catalysts, leading to the formation of polymeric hydrocarbons [1], has been studied by a number of investigators [2-11].

We carried out an investigation comparing the decomposition of diazomethane, diazoethane, diazotoluene, and diazodiphenylmethane and their mixtures in the presence of metallic copper and certain boron compounds (trimethyl borate or boron trifluoride).

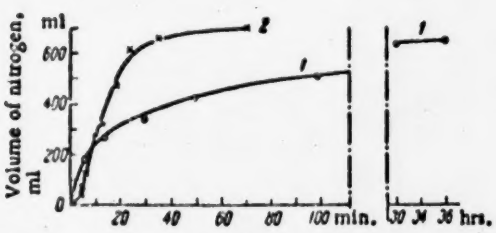


Fig. 1. Rate of evolution of nitrogen during the decomposition of diazomethane (1.4 g): 1) in the presence of metallic copper (1 g), 2) in the presence of trimethyl borate (0.3 g). Concentration of diazomethane, 0.85 g in 100 ml of solution.

The decomposition of diazomethane in the presence of trimethyl borate was distinguished by the presence of an induction period, as may be seen from Figure 1. Moreover, an essential difference in the action of these catalysts is that trimethyl borate causes rapid decomposition of the diazomethane and leads to quantitative formation of polymethylene, $(CH_2)_x$. Only nitrogen is present in the gaseous products, and hydrocarbons are totally absent. In the case of copper, the yield of polymers comprises only 10-15%, the nitrogen contains ethylene, and, in addition, various nitrogen-containing products are formed. It can be assumed that the reaction forming polymethylene from diazomethane is an ionic process having certain traits in common with the polymerization of olefinic hydrocarbons under the influence of ionic catalysts.

Diazoethane also decomposes in the presence of copper forming the corresponding polymeric hydrocarbon. The yield of polyethylidene comprises 40%, i.e., it is higher than that during the decomposition of diazomethane.

Diazotoluene, in the presence of boron trifluoride etherate, forms only the azine of benzaldehyde, and liberates nitrogen. We note, in passing, that the formation of the corresponding azines was also observed during the decomposition of diazomethane and diazoethane; however, they were obtained only in small amounts.

Diazodiphenylmethane, in the presence of boron trifluoride, forms only the azine of benzophenone, and liberates nitrogen.

We also prepared copolymers by the decomposition of a mixture of diazomethane and diazoethane in the presence of trimethylborate and by the decomposition of a mixture of diazomethane and diazotoluene in the presence of boron trifluoride. It developed that, in this case, a mixture of products was formed consisting of polymethylene, the corresponding copolymer, and a mixture of the corresponding azines.

During the decomposition of mixtures of diazomethane and diazoethane, copolymers were formed which, depending on the quantitative ratio of the starting materials, consisted of polymethylene with various numbers of methyl side chains.

This copolymer can be considered as the analog of high-pressure polyethylene when the number of methyl side chains is small. With different monomer ratios, the copolymer obtained can be considered as the analog of polypropylene.

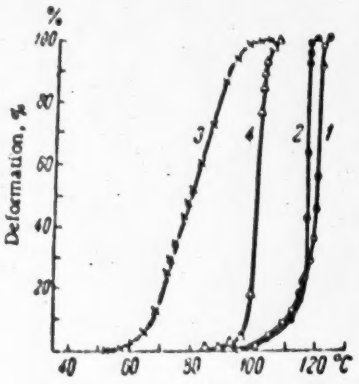


Fig. 2. Polymer deformation in relation to temperature at a constant load (100 g/4 mm) and a heating rate of 75° per hour.

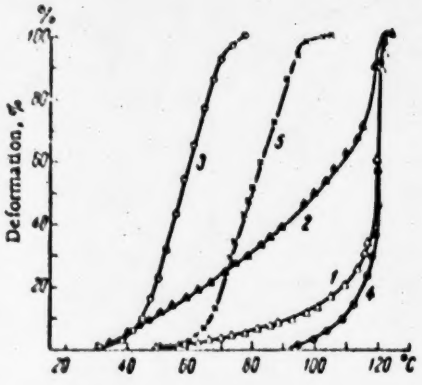


Fig. 3. Polymer deformation in relation to temperature at a constant load (100 g/4 mm) and a heating rate of 75° per hour.

In Figure 2 are presented the thermomechanical properties of the polymethylene produced in the presence of copper (Curve 1) and, for comparison, a low-pressure polyethylene produced in the presence of triethyl aluminum (2). In this same figure are presented the curves for the polyethylidene produced in the presence of copper (3) and a high-pressure polyethylene (4).

As may be seen from Figure 2, the curves for polymethylene from diazomethane (1) and low-pressure polyethylene partically coincide, which indicates that they have the same structure. The curve for polyethylidene lies considerably to the left, and shows that the structure of this polymer is totally different from those of the remaining polymers. The curve for the high-pressure polyethylene occupies an intermediate position, thereby indicating the presence of side chains.

An x-ray investigation of the polymethylene obtained from diazomethane and the low-pressure polyethylene showed that both are crystalline products with crystallinities up to 90-100%. In contradistinction to these products, the high-pressure polyethylene proved to be partially amorphous. The x-ray picture of polyethylidene also indicated this polymer to be partially crystalline, the crystallinity amounting to 25%.

In Figure 3 are presented the thermomechanical curves for copolymers prepared in the presence of copper from diazomethane and diazoethane at different proportions of the latter (1 – with 3%, 2 and 3 – with 74% diazoethane); also presented for comparison are the curves for polymethylene prepared from diazomethane (4) and for polyethylidene prepared from diazoethane (5). As may be seen from this figure, the curve for the copolymer prepared with 3% diazoethane shows initial softening at the same temperature as for polyethylidene prepared from diazoethane alone (5), and later on it approximates the curve for polymethylene. In this is seen the influence of the available methyl groups; however, a similarity with high-pressure polyethylene is not apparent (see Figure 2). This is explainable on the basis that high-pressure polyethylene is a polymer with a branched macromolecule, while our copolymer has only short methyl groups.

A part of the product obtained by the decomposition of a mixture of 74 mole % diazoethane and 26 mole % diazomethane was soluble in ether. Thermomechanical curves were plotted both for the soluble and for the insoluble part of the copolymer.

Curve 2 (Figure 3) corresponds to copolymer prepared with 74% diazoethane and represents the ether-insoluble part of the product. This curve, just as the curve for the soluble portion of the polymer (3) prepared

with these proportions, shows an initial softening at a lower temperature. However, the further courses of these curves differ; the curve for the soluble portion of the copolymer (3) is similar in form to the curve for polyethylidene, differing only in the lower softening temperature. The curve for the insoluble copolymer (2) is, in general, similar to the curve for the copolymer prepared with 3% diazoethane, and it coincides at its end with the curve for polymethylene prepared from diazomethane alone.

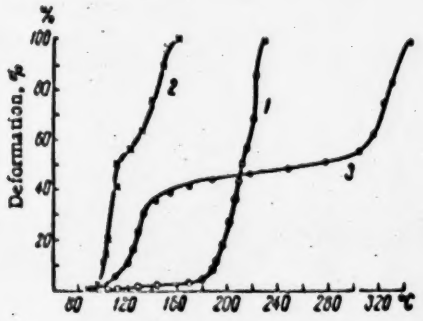


Fig. 4. Polymer deformation in relation to temperature at a constant load (100 g/4 mm) and a heating rate of 75° per hour.

In Figure 4 are presented the thermomechanical curves for a polystyrene (1) prepared by copolymerization of diazomethane and diazotoluene in the presence of boron trifluoride, for a polystyrene prepared by a free radical-initiated mass polymerization of styrene (2), and the polymethylene prepared in the presence of boron trifluoride etherate (3). As may be seen from this figure, the polystyrene formed during the copolymerization of diazomethane and diazoethane has a high melting point (of the order of 220-224°); moreover, it is insoluble in ether and heptane, and is similar to "isotactic" polystyrene [12].

It is impossible to connect the formation of an unbranched, ordered polystyrene under our conditions with the orienting effect of a crystal surface of the catalyst, as has been done by Natta [12] and other investigators [13].

Apparently, a more correct concept is that the reason for the ordered distribution of the substituents in a molecule of this polystyrene is the ordering effect of the side chains during the process of polymer formation. This self-ordering effect depends, first of all, on the steric effect of the groups, an effect which is, in general, analogous to that observed during the polymerization of vinyl type monomers. We have proposed to designate this steric effect as "stereochemical factor", understanding by this the sum total of the steric effects which are dependent on the size of the substituents and dictated by their volume [15-17]. This effect first appeared during polymerization and copolymerization of monomers, and, therefore, this aspect was previously considered by us in detail for a large number of examples [15]. Obviously, we must now supplement these concepts by taking into account the effects of the substituents on the order of combination of the units in the macromolecule of the polymer. During the disposing of the phenyl groups one after the other, as occurs in the case of polystyrene, the addition of each succeeding radical, which contains a phenyl group, must proceed with an arrangement of the phenyl group in space such that there is no hindrance from the direction of the phenyl groups already present; it is easily noted that in such a case the phenyl groups are arranged along the outside of a spiral.

The fact that in free radical polymerization there is no such ordered disposition of the substituents can be explained on the basis that a free radical, which is just what the terminal carbon atom of a growing macromolecule is, has a planar configuration, and its transition to a tetrahedral structure is equally probable in either direction, so that the configuration of the polymer which is formed is a case of equally probable distribution of substituents in various positions leading to the absence of order in the distribution of the substituents and to the formation of a polymer with a low melting point.

In the case of the formation of the copolymer from diazomethane and diazotoluene, we have an ionic process, and this guarantees retention of the same configuration of carbon atoms in the final copolymer. In the case of the copolymer from diazomethane and diazoethane, the formation of an isotactic copolymer is not observed; this is obviously due to the fact that the methyl groups are not large enough for their interaction to provide the self-ordering effect.

Proof of the presence of steric hindrance is also apparent in the fact that the joint decomposition of a mixture of diazomethane and diazodiphenylmethane does not lead to the production of a copolymer. Only the azine of benzophenone and polymethylene are formed.

LITERATURE CITED

[1] E. Bamberger and F. Tshirner, Ber., 33, 955 (1900).

[2] H. Meerwein and H. Rathjen, Ber., 75, 1610 (1942).

[3] L. Leitch, P. Gagnon and A. Cambron, Can. J. Res., 28B, 256 (1950).

[4] G. Buckley, L. Cross and N. Ray, J. Chem. Soc., 1950, 2714.

[5] C. Bawn and T. Rhodes, Trans. Farad. Soc., 50, 934 (1954).

[6] H. Meerwein, Angew. Chem., 60A, 78 (1948).

[7] G. Buckley and N. Ray, J. Chem. Soc., 1952, 3701.

[8] L. Kantor and R. Osthoff, J. Am. Chem. Soc., 75, 931 (1953).

[9] K. Hamann, Zs. Elektrochem., 60, 317 (1956).

[10] P. Plesch, Zs. Elektrochem., 60, 325 (1956).

[11] L. Feltzin, A. Restaino and R. Mesrobian, J. Am. Chem. Soc., 77, 208 (1955).

[12] G. Natta, Angew. Chem., 68, 303 (1956).

[13] C. F. Schildknecht, S. T. Cross, H. K. Devidson and I. M. Laubent, Ind. and Eng. Chem., 40, 2104 (1943).

[14] V. V. Korshak, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1949, 269.

[15] V. V. Korshak, The Chemistry of Highmolecular Compounds,* Izd. AN SSSR, 1950, p. 178.

[16] V. V. Korshak and N. G. Matveeva, Proc. Acad. Sci. USSR, 85, 797 (1952).

Institute of Heteroorganic Compounds
Academy of Sciences USSR

Received March 15, 1957

* In Russian.

HALOCHROMISM OF PHENYL- AND CYCLOHEXYLCARBINOLS

V. F. Lavrushin and N. N. Verkhovod

(Presented by Academician A. N. Nesmeyanov, April 9, 1957)

In studying the phenomenon of halochromism in carbinols of various structures [1-3], we established that acid solutions of these compounds give two types of absorption spectra. Carbinols containing phenyl radicals are characterized by complex absorption curves with three or more absorption bands, while the absorption curves for tertiary cyclohexanols and aliphatic alcohols have only one absorption band and a broad inflection in the near visible spectrum.

In this connection, it was of interest to study the absorption spectra of acid solutions of aromatic alcohols and their variation with respect to the degree of substitution of cyclohexyl radicals for benzene rings in the molecule. With this aim, we undertook a study comparing the absorption spectra of triphenylcarbinol, cyclohexyldiphenylcarbinol, dicyclohexylphenylcarbinol, tricyclohexylcarbinol, methyldicyclohexylcarbinol, and dicyclohexylcarbinol.

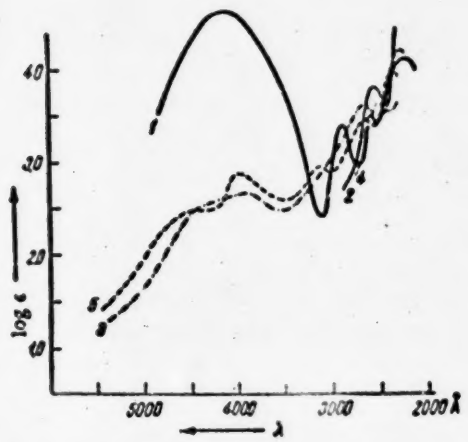


Fig. 1. Triphenylcarbinol; 1) in conc. H_2SO_4. Cyclohexyldiphenylcarbinol; 2) in C_2H_5OH; 3) in conc. H_2SO_4. Dicyclohexylphenylcarbinol; 4) in C_2H_5OH; 5) in conc. H_2SO_4.

Triphenylcarbinol. The absorption spectra of sulfuric acid solutions of triphenylcarbinol have been studied repeatedly [4,5]. According to our data [2], the absorption curve of such a solution has four bands (Figure 1, 1): I) λ = 4200 A, ε = 50000; II) λ = 2900 A, ε = 3100; III) λ = 2600 A, ε = 400 and IV) λ = 2280 A, ε = 16000.

Cyclohexyldiphenylcarbinol in solution in ethyl alcohol yields an absorption curve with a single band, the maximum of which is located at λ = 2530 A and ε = 7762. The curve for the sulfuric acid solution has a complex outline and is composed of three absorption bands (Figure 1,3): I) λ = 393 A, ε = 467; II) λ = 266 A, ε = 398; III) λ = 230 A, ε = 15140.*

In contrast to the curve for triphenylcarbinol, here the band in the visible spectrum is considerably less intense and has a broad inflection at its long-wave end. At the wave length of the second triphenylcarbinol band, the curve rises over a broad region of the spectrum and is capped in the middle and short ultraviolet by two absorption bands characteristic of aromatic carbinols [2].

Dicyclohexylphenylcarbinol in alcohol solution also absorbs in the ultraviolet region of the spectrum and has a single absorption band with its maximum at λ = 2680 A and ε = 3311. In concentrated sulfuric acid, it forms a turbid, orange-yellow solution, which clears up completely after heating for 15 minutes on a water bath. The absorption curve of the sulfuric acid solution extends over a broad region of the spectrum and includes five bands (Figure 1,4): I) λ = 442 A, ε = 316; II) λ = 398 A, ε = 776; III) λ = 317 A, ε = 851; IV) λ = 287 A, ε = 2818; V) λ = 237 A, ε = 8128.* The first two long-wave bands are located in the region of the broad long-

* Values for λ are given as they appear in original text – Publisher's note.

wave band of triphenylcarbinol. Two other bands are somewhat displaced in the direction of the visible spectrum. The band at the shortest wave length almost coincides with the triphenylcarbinol band.

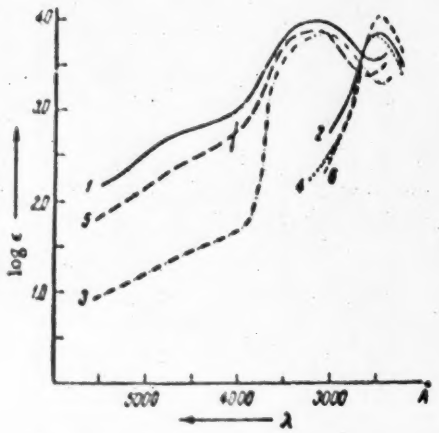


Fig. 2. Tricyclohexylcarbinol: 1) in conc. H_2SO_4; 2) after dilution with C_2H_5OH. Methyldicyclohexylcarbinol: 3) in conc. H_2SO_4; 4) after dilution with C_2H_5OH. Dicyclohexylcarbinol: 5) in conc. H_2SO_4; 6) after dilution with C_2H_5OH.

Tricyclohexylcarbinol immediately gives a yellow color on interaction with concentrated sulfuric acid. The solution becomes completely transparent on heating on a water bath for 10 minutes. Under u. v. light, such a solution has a strong light green fluorescence.

The absorption curve of the sulfuric acid solution (Figure 2,1) differs sharply from the curves presented above for carbinols containing phenyl radicals. In the 5500-3800 A region there is a sloping inflection, after which comes a broad absorption band with a maximum at λ = 3050 A and ϵ = 8913.

Methyldicyclohexylcarbinol forms with concentrated sulfuric acid a turbid yellow solution, which becomes clear with short heating on a water bath. It has an intense light green fluorescence under ultraviolet irradiation.

The absorption curve of the sulfuric acid solution (Figure 2,3) consists of a sloping, long-wave branch and a broad absorption band with a maximum at λ = 3000 A and ϵ = 6300.

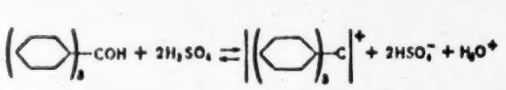
Dicyclohexylcarbinol also forms with concentrated sulfuric acid a turbid yellow solution, which clears up completely after heating on a water bath for 10 minutes. It displays an intense light green fluorescence under u. v. light.

The absorption curve of the sulfuric acid solution of this carbinol (Figure 2,5), in common with those of the other cyclohexylcarbinols, has a long-wave inflection which enters the visible region of the spectrum and a single broad absorption band with a maximum at λ = 3090 A and ϵ = 7078.

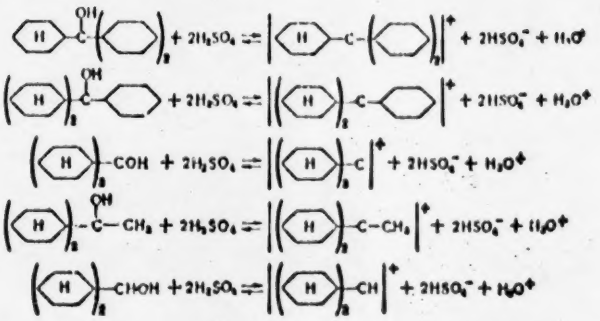
Thus, as a result of this study of the absorption spectra of solutions of phenyl- and cyclohexylcarbinols in concentrated sulfuric acid, it appears that triphenylcarbinol, cyclohexyldiphenylcarbinol, and dicyclohexylphenylcarbinol have one type of complex absorption spectrum, the curves of which differ among themselves in the number of absorption bands. From sulfuric acid solutions of tricyclohexylcarbinol, methyldicyclohexylcarbinol, and dicyclohexylcarbinol there is obtained another type of absorption spectrum, characterized by a simpler form of the curves which have a single absorption band.

The appearance of color during the reaction of all of the carbinols studied by us with concentrated sulfuric acid and its disappearance on dilution of the acid solutions with water indicates that we are concerned in this case with a typical halochromic phenomenon.

The phenomenon of halochromism of triphenylcarbinol has been well studied [6], and is an acid-base reaction:



Since other phenyl- and cyclohexylcarbinols behave, with respect to sulfuric acid, as does triphenylcarbinol, it can be assumed that their reaction with the acid proceeds in an analogous manner.



The different number of bands on the absorption curves of carbinols containing phenyl radicals depends on the number of these radicals, and was observed by us previously [2] during a study of halochromism of aromatic carbinols. It is of interest that in the case of carbinols which do not contain phenyl radicals, the absorption curves, with respect to form and position, almost coincide with each other and with the curves of tertiary cyclohexanols and aliphatic alcohols [1,3]. This, in our opinion, is additional confirmation that the curves of all these compounds result from the carbonium ion $\rangle C^+$, since the radicals bonded to it do not absorb in the ultraviolet.

LITERATURE CITED

[1] V. F. Luvrushin, N. N. Verkhovod and P. K. Movchan, Proc. Acad. Sci. USSR, 105, 723 (1955).

[2] V. F. Lavrushin, J. Gen. Chem., 26, 2697 (1956).*

[3] V. F. Lavrushin and N. N. Verkhovod, J. Gen. Chem., 26, 2704 (1956).*

[4] L. C. Anderson, J. Am. Chem. Soc., 52, 4567 (1930).

[5] C. S. Schoepfle and J. D. Rian, J. Am. Chem. Soc., 54, 3687 (1932).

[6] L. P. Hammett, Physical Organic Chemistry, N. Y., 1940, p. 54.

A. M. Gorky Kharkov
State University

Received April 9, 1957

* Original Russian pagination. See C. B. Translation.

BLANK
PAGE

BETA-CYANOVINYL KETONES

Academician A. N. Nesmeyanov and M. I. Rybinskaya

In our previous work, a joint effort with N. K. Kochetkov, the varied use of β-chlorovinyl ketones for the preparation of heterocyclic systems was demonstrated [1]. Synthesis of the corresponding cyanides would, obviously, broaden these opportunities. Although the chlorine atom in β-chlorovinyl ketones undergoes nucleophilic substitution [2] in spite of its vinyl position, and, for example, the corresponding iodides and thiocyanates are readily prepared by exchange, it has not been possible to exchange with cyanide salts [3]. The reaction does not go in non-polar media, and tars are formed in polar media.

We have been able to prepare β-cyanovinyl ketones through β-acylvinyltrialkylammonium salts [4-6]. The latter are easily formed by the action of β-chlorovinyl ketones on tertiary amines.

$$RCOCH=CHCl + N(R_1)_3 \rightarrow RCOCH=CH\overset{+}{N}(R_1)_3\,\overline{Cl}.$$

Under the action of potassium cyanide in aqueous solution, β-acylvinyltrialkylammonium salts exchange the trialkylammonium group for cyanide. Thus, β-benzoylvinyltriethylammonium chloride in aqueous medium readily reacts with potassium cyanide with the formation of phenyl β-cyanovinyl ketone (yield 77% of theoretical) and triethylamine. Other aryl β-cyanovinyl ketones were prepared in good yields by this same route.

$$\rightarrow ArCOCH=CH\overset{+}{N}(C_2H_5)_3\,\overline{Cl} + KCN \rightarrow [ArCOCH=CH\overset{+}{N}(C_2H_5)_3\,\overline{CN}] \rightarrow$$

$$\rightarrow ArCOCH=CHCN + N(C_2H_5)_3,$$

where Ar = C_6H_5-, O—ClC_6H_4—, p-BrC_6H_4—.

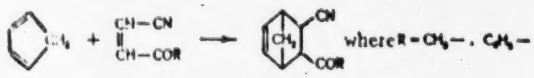
The reaction was carried out in water-ether or water-benzene medium in order to provide for more rapid removal of the aryl β-cyanovinyl ketone from the alkaline solution, the aryl β-cyanovinyl ketone passing into the organic layer as it was formed.

Alkyl β-cyanovinyl ketones could be prepared only by the action of potassium cyanide on aqueous solutions of β-acylvinyltrimethylammonium chlorides. The reaction with potassium cyanide was carried out in water-benzene medium. The resulting β-acylvinyltrimethylammonium cyanide readily decomposes on heating on a water bath, and trimethylamine is liberated as a gas from the reaction mixture. Moreover, it is important to note that the reaction must be carried out in a buffered solution of trimethylamine hydrochloride, since alkyl β-cyanovinyl ketones undergo very rapid change under the action of aqueous solutions of alkalies. We prepared methyl, ethyl, and propyl β-cyanovinyl ketones by this method; however, the yields were lower than for the aryl β-cyanovinyl ketones.

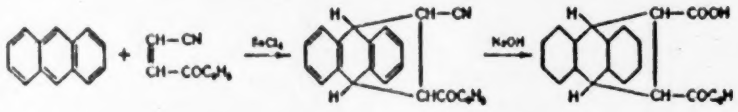
This variant was also used for the synthesis of aryl β-cyanovinyl ketones, the only difference being that the use of cooling gave more satisfactory results. In this case, phenyl β-cyanovinyl ketone was obtained in

almost quantitative yield in a satisfactorily pure state. It is also interesting to note that p-nitrophenyl β-cyanovinyl ketone was obtained by this method, while the method based on the use of triethylamine failed.

The structure of these cyanovinyl ketones was confirmed by the following reactions. The β-cyanovinyl ketones give semicarbazones. Owing to the presence of an active double bond, they readily undergo Diels-Alder reactions. Methyl and phenyl β-cyanovinyl ketones react with cyclopentadiene yielding the corresponding addition products.



The 2-benzoyl-3-cyanobicyclo(2,2,1)-5-heptene formed as a result of this reaction was hydrolyzed to the corresponding acid. In addition, the product of the addition of phenyl β-cyanovinyl ketone to anthracene was prepared in the presence of stannic chloride [7]. This addition product was hydrolyzed to β-benzoyl-α,β-endo-9,10-dihydroanthracenepropionic acid, previously obtained by Barnett and co-workers [8].



Thus, we have established that quaternary β-acylvinylammonium salts can be used in ketovinylation reactions. This is confirmed by the fact that the reaction of β-propionylvinyltrimethylammonium chloride with sodium sulfide leads to bis(β-propionylvinyl) sulfide in good yield.

$$C_2H_5COCH=CH\overset{+}{N}(CH_3)_3\overset{-}{Cl} + Na_2S \rightarrow (C_2H_5COCH=CH)_2S + N(CH_3)_3 + NaCl.$$

EXPERIMENTAL

Alkyl β-cyanovinyl ketones. About 10 ml of liquid trimethylamine was added to a solution of 0.1 mole of alkyl β-chlorovinyl ketone in 100 ml of absolute acetone while stirring and cooling with solid carbon dioxide. The reaction mixture was allowed to stand for 30 minutes at room temperature; the precipitate was then filtered and rapidly and carefully washed with absolute acetone. The yield of β-acyltrimethylammonium chloride was almost quantitative (β-acetylvinyltrimethylammonium chloride; m.p. 135-136°).

Found %: C 51.30; H 8.66; Cl 21.64; N 8.39. $C_7H_{14}ONCl$. Calculated %: C 51.37; H 8.62; Cl 21.71; N 8.56.

The quaternary salt separated from the reaction mixture was used without further purification for the synthesis of the β-cyanovinyl ketones. The previously prepared β-acylvinyltrimethylammonium chloride, 150 ml benzene, and 0.1 mole of potassium cyanide were added to a solution of 5 g of trimethylamine hydrochloride in 5 ml of water. The reaction mixture was stirred vigorously and heated on a water bath. When the temperature of the bath reached 50-60°, a solution of 0.95 mole of potassium cyanide in 15 ml of water was added dropwise to the solution. The evolution of gaseous trimethylamine was observed with the first drops of the potassium cyanide solution. With the cessation of the turbulent foaming, the benzene layer was carefully decanted, and a new portion of benzene (100 ml) was added to the flask. Heating and stirring were continued. After an hour, the entire operation was repeated; the process was repeated 3-4 times. The combined benzene solutions were dried over sodium sulfate, and, after distillation of the benzene, the product was distilled under vacuum. The major fraction was alkyl β-cyanovinyl ketone. Their semicarbazones were prepared by the usual method and were recrystallized from alcohol (Table 1).

TABLE 1

Alkyl β-cyanovinyl ketones and their semicarbazones	MR_D found	MR_D calc.	Yield, %	C, % found	C, % calc.	H, % found	H, % calc.	N, % found	N, % calc.
$CH_3COCH=CHCN$, b.p. 73/11 mm, m.p. 27° n_D^{20} 1.4590; d_4^{27} 1.0050	25.87	24.65	40.3	62.86	63.15	5.41	5.26	14.03	14.73
Semicarbazone, m.p. 227-228° (with decomp.)	--	--	--	47.37	47.36	5.48	5.26	36.04	36.84
$C_2H_5COCH=CHCN$, b.p. 77/8 mm n_D^{20} 1.4620; d_4^{20} 0.9814	30.57	29.27	21.7	65.79	66.03	6.62	6.42	12.87	12.84
Semicarbazone, m.p. 187-188° (with decomp.)	--	--	--	50.61	50.60	6.95	6.02	33.79	34.07
$C_3H_7COCH=CHCN$, b.p. 85-85.5°/8 mm n_D^{20} 1.4594; d_4^{20} 0.9593	35.14	33.88	54.6	68.12	68.29	7.46	7.33	11.42	11.38
Semicarbazone, m.p. 158-159°	--	--	--	53.04	53.33	6.53	6.66	31.06	31.11

Aryl β-cyanovinyl ketones. Variant A. To a solution of 5 g of trimethylamine hydrochloride in 5 ml of water was added the quaternary ammonium salt prepared from 0.1 mole of aryl β-chlorovinyl ketone and 10 ml of liquid trimethylamine according to the above-described method. 100-150 ml of benzene was then added, and, while stirring and cooling, a solution of 0.15 mole of potassium cyanide in 30 ml of water was added dropwise. After an hour, the benzene layer was decanted, and a new portion of benzene (50 ml) was added. This operation was repeated 3 times. The combined benzene solutions were washed with 5% hydrochloric acid, and, after drying over sodium sulfate, the benzene was removed under vacuum. The remaining crystalline material was aryl β-cyanovinyl ketone (Table 2).

TABLE 2

Aryl β-cyanovinyl ketone	Yield, % Var A	Yield, % Var B	M.p. °C	C, % found	C, % calc.	H, % found	H, % calc.	N, % found	N, % calc.	Hal, % found	Hal, % calc.
$C_6H_5COCH=CHCN$ *	94	8.9	82	76.47	76.43	4.65	4.46	8.99	8.98	--	--
o-$ClC_6H_4COCH=CHCN$	97	50.0	140-143	62.66	62.64	3.19	3.13	7.12	7.31	18.68	18.53
p-$BrC_6H_4COCH=CHCN$	77	44.0	155-156.5	51.09	50.82	2.65	2.54	5.75	5.94	34.05	33.87
p-$NO_2C_6H_4COCH=CHCN$	77	--	147-150	59.17	59.45	3.01	2.97	--	--	--	--

* Semicarbazone, prepared by the usual method, decomposition temperature 183° (from alcohol).

Found %: C 56.84; H 5.25; N 23.93. $C_{11}H_{10}ON_4 \cdot H_2O$. Calculated %: C 56.89; H 5.17; N 24.13.

Variant B. 10.1 g of triethylamine was added slowly to 0.1 mole of aryl β-chlorovinyl ketone in 50 ml of absolute acetone while cooling. After 1.5-2 hours, the resulting precipitate of β-arylvinyltriethylammonium chloride was filtered and quickly washed with absolute acetone. This salt was dissolved in 30 ml of water, 200 ml of ether or benzene was added, and, while stirring vigorously and cooling with dry ice, a solution of 0.51 mole of potassium cyanide in 50 ml of water was added dropwise. The corresponding aryl β-cyanovinyl ketones were obtained by further treatment as described under Variant A (see Table 2).

2-Acetyl-3-cyanobicyclo(2,2,1)-5-heptene. 1.5 g of cyclopentadiene was added to a solution of 2 g of methyl β-cyanovinyl ketone in 10 ml of dry benzene. After spontaneous heat evolution had ceased, the mixture was heated for 2 hours on a water bath. On the following day, after distillation of the benzene, the residue was distilled under vacuum. The yield was 2.3 g (68% of theoretical), b.p. 145-146°/13-12 mm. The material was a yellowish, viscous liquid; n_D^{20} 1.4962; d_4^{20} 1.091. MR_D found 43.18. MR_D calculated 43.34.

Found %: C 74.60; H 6.94; N 8.83. $C_{13}H_{11}ON$. Calculated %: C 74.53; H 6.83; N 8.80.

2-Benzoyl-3-cyanobicyclo(2,2,1)-5-heptene. This compound was prepared similarly from 2 g of phenyl β-cyanovinyl ketone and 1 g of cyclopentadiene in 5 ml of dry benzene. The yield was 1.8 g (64.3% of theoretical), m. p. 87-88° (from alcohol).

Found %: C 80.81; H 5.74; N 6.34. $C_{15}H_{13}ON$. Calculated %: C 80.71; H 5.83; N 6.27.

2-Benzoylbicyclo(2,2,1)-5-heptene-3-carboxylic acid. A mixture of 0.48 g of 2-benzoyl-3-cyanobicyclo(2,2,1)-5-heptene, 0.2 g of potassium hydroxide, 5 ml of alcohol, and 2 ml of water was heated on a water bath to the complete cessation of the liberation of ammonia. The reaction mixture was diluted with water and filtered. The filtrate was acidified with hydrochloric acid, and the liberated oil was extracted with ether. The ethereal extract was washed with water, and, after drying over sodium sulfate, the ether was distilled. The residue was an oil which was crystallized by friction. The yield was 0.4 g (76.9% of theoretical), m. p. 108-109° (from aqueous alcohol).

Found %: C 74.38; H 5.83. $C_{15}H_{14}O_3$. Calculated %: C 74.37; H 5.78.

β-Benzoyl-α,β-endo-9,10-dihydroanthracenepropionitrile. To a solution of 1 g of phenyl β-cyanovinyl ketone in 30 ml of dry benzene was added 1.13 g of anthracene and 2 g of anhydrous stannic chloride. The mixture was heated to boiling for 15 minutes and decomposed with dilute hydrochloric acid. The benzene layer was decanted, and the aqueous layer was extracted with benzene. The benzene solution was washed with water, dried over sodium sulfate, and the benzene was evaporated under vacuum. The residue, after recrystallization from benzene, amounted to 1.7 g (yield 73.8% of theoretical), m. p. 203-204°.

Found %: C 86.10; H 5.12; N 4.02. $C_{24}H_{19}ON$. Calculated %: C 85.94; H 5.07; N 4.17.

The β-benzoyl-α,β-endo-9,10-dihydroanthracenepropionitrile, on hydrolysis with alcoholic alkali, gave β-benzoyl-α,β-endo-9,10-dihydroanthracenepropionic acid, m. p. 232° (from alcohol).

Literature data [8]: m. p. 234°. A mixed sample showed no melting point depression.

Bis(β-propionylvinyl) sulfide was prepared by the addition of a solution of 0.1 mole of sodium sulfide to a solution of 0.2 mole of β-propionylvinyltrimethylammonium chloride in water. The yield was 88.13%, m. p. 80° (from alcohol).

Found %: C 63.72; H 7.94; S 14.36. $C_{12}H_{18}O_2S$. Calculated %: C 63.71; H 7.96; S 14.15.

LITERATURE CITED

[1] For references, see A. N. Nesmeyanov, M. I. Rybinskaya and N. K. Belsky, Proc. Acad. Sci. USSR, 113, No. 2, 343 (1957).*

[2] N. K. Kochetkov, Proc. Acad. Sci. USSR, 82, No. 4, 593 (1952).

[3] L. Panizzi, Gaz. Chim. Ital., 77, 549 (1947).

[4] A. Ya. Yakubovich and E. N. Merkulova, J. Gen. Chem., 16, 55 (1946).

[5] V. T. Klimko, A. Ya. Khorlin, et al., J. Gen. Chem., 27, No. 7, 62 (1957).*

[6] C. J. Cavallito, J. Am. Chem. Soc., 77, No. 15, 4159 (1955).

[7] A. N. Nesmeyanov, M. I. Rybinskaya and N. K. Kochetkov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1955, 817.*

[8] E. B. Barnett, N. F. Goodway, A. G. Higgins and C. A. Lawrence, J. Chem. Soc., 1934, 1224.

Institute of Heteroorganic Compounds
Academy of Sciences USSR

Received March 12, 1957

*Original Russian pagination. See C.B. Translation.

TRANSFORMATIONS IN TERNARY SOLID SOLUTIONS BASED ON Ni_3Fe

M. P. Ravdel and Ya. P. Selissky

(Presented by Academician I. P. Bardin, March 13, 1957)

The specific effect of molybdenum on the degree of order in alloys approximating Ni_3Fe in composition has previously been noted [1-4]. It was observed that alloying with molybdenum changes in principle the nature of the conversion during annealing of these alloys, this change appearing as an anomaly in the electrical resistance and differing from the ordering of volume effects. In the present work, the effect of elements of varying natures, Mn, Si, Cu, Mo, Cr, V, and W, on the ordering process of Ni_3Fe alloys was investigated.

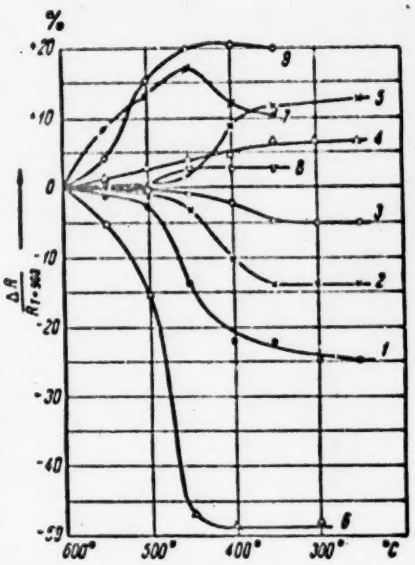


Fig. 1. Change in the electrical resistance of Ni-Fe alloys alloyed with various elements in relation to quench temperature: 1) Ni_3Fe alloy; 2) Fe-Ni (79% Ni); 3) $Ni_3(Fe,Cu)$; 4) $Ni_3(Fe,Cr)$; 5) $Ni_3(Fe,Mo)$; 6) $Ni_3(Fe,Mn)$; 7) $Ni_3(Fe,Si)$; 8) $Ni_3(Fe,W)$ 9) $Ni_3(Fe,V)$.

In Figure 1 is shown the change in the electrical resistance of alloys with various alloying components in relation to quench temperature in a step-wise cooling process. The initial state of all alloys was obtained by quenching from 900° in water. Soaking time varied from 24 to 120 hours, depending on the quench temperature.

Alloying Mn (3%) significantly increased the effect of order observable in the Ni_3Fe alloy without an additional alloying element, and appreciably increased the temperature of the order-disorder transformation. Alloying Cu (5%) decreased the ordering effect, acting in the same manner as a deviation from stoichiometric composition in the binary Fe-Ni system (for example, the alloy with 79% Ni).

In alloys containing Mo (5%), Cr (5%), V (4%), and W (4%), an anomalous increase in electrical resistance was observed after lengthy step-wise thermal treatment, this increase amounting to 6.5% for the alloy with Cr, 12% for the alloy with Mo, and 20% for the alloy with V. The increase in electrical resistance was comparatively small (2.5%) for the alloy containing W. An electrical resistance anomaly was also apparent in the alloy containing 3% Si, the curve having a maximum at 450°.

In Figure 2 are presented curves showing the variation in coefficient of thermal expansion, α, with temperature for some of the alloys investigated. The initial state was obtained by lengthy step-wise cooling in the temperature range from 550 to 250°. The curves for the Ni_3Fe and $Ni_3(Fe,Mn)$ alloys (Figure 2, a and b) are characterized by the presence of A-shaped maxima. Maxima of similar shape have been observed [5] on the temperature-heat capacity curves of ordered samples of Ni_3Fe alloy during disorder transformations. From a comparison of these curves, it is seen that the temperature

of the order-disorder transformation for the $Ni_3(Fe,Mn)$ alloy is higher than that for the Ni_3Fe alloy. The introduction of Cu causes considerable washing out of the maximum on the curve (Figure 2,c) and a decrease in the temperature of the transformation to 450°, which, obviously, is connected with concentration disorder.

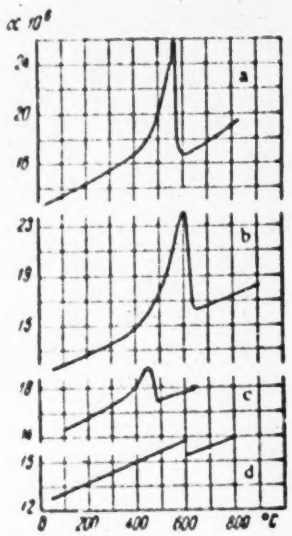


Fig. 2. Dependence of coefficient of thermal expansion (α) on temperature: a) Ni_3Fe alloy; b) $Ni_3(Fe,Mn)$; c) $Ni_3(Fe,Cu)$; d) $Ni_3(Fe,V)$.

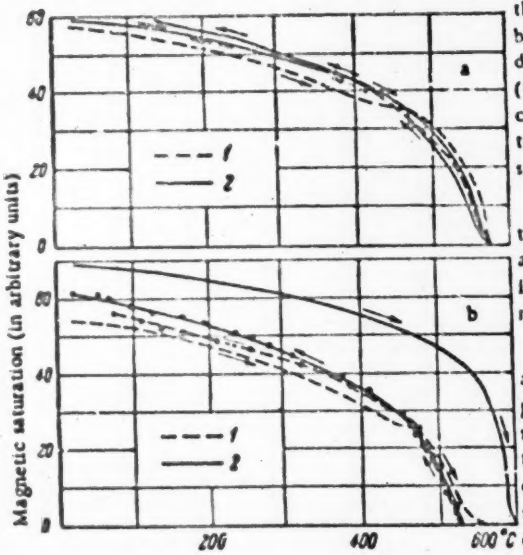


Fig. 4. Thermomagnetic heating and cooling curves: a) Ni_3Fe alloy; b) $Ni_3(Fe,Mn)$, 3% Mn; 1) after quenching in water from 900°; 2) after stepwise thermal treatment.

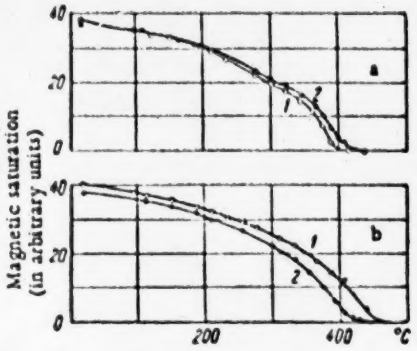


Fig. 3. Thermomagnetic heating and cooling curves for the alloy $Ni_3(Fe,V)$, 4% V: a) after quenching from 900° in water; b) after step-wise treatment; 1) heating 2) cooling.

The curve of Figure 2, d was obtained for the $Ni_3(Fe,V)$ alloy; however, curves for alloys with Mo and Cr have exactly this same shape. All of these curves i.e., for the V, Mo, and Cr alloys are characterized by the absence of maxima peculiar to disordered alloys and by the presence of breaks in the continuity of the dependence of α on temperature. The highest temperature (~600°) for a discontinuity break was observed in the case of alloys containing V, a somewhat lower temperature (~520°) was observed for the alloy with Mo, and a still lower temperature (~520°) for the alloy with Cr.

In Figure 3 are presented thermomagnetic curves typical of alloys containing one of the elements giving an electrical resistance anomaly (V, Mo, and Cr), and in Figure 4, for comparison, are presented thermomagnetic curves for the ordered alloys Ni_3Fe and $Ni_3(Fe,Mn)$.

The thermomagnetic curves for alloys exhibiting an electrical resistance anomaly and an anomalous temperature-thermal expansion coefficient relationship are similar, and are characterized by an indistinct magnetic transformation during heating and cooling. The latter can be explained by local chemical disorder of the solid solution. Apparently, at specific temperatures, chemical complexes, differing by a higher Curie point, are formed about the foreign atoms by virtue of the appearance of a chemical affinity exhibited by them for the atoms of the basic components of the solid solution. This is confirmed by the fact that the Curie point of the quenched alloy is significantly lower than the Curie

point of the alloy subjected to lengthy step-wise cooling (see Figure 3). In all cases, the Curie point of the quenched sample is significantly higher during cooling than during heating (Figure 3, a). This indicates that the rate of formation of these complexes during the cooling process is greater than the rate of ordering of the Ni_3Fe alloy.

The more the alloying element differs in nature from the basic elements making up the solid solution — from iron and nickel — the stronger the chemical affinity and the more stable the complexes formed in the solid solution. It is possible to confirm this proposition by means of the greater effect of V in comparison to that of Cr and even of Mo.

The peculiar effect of Mn is apparently connected with the participation in the magnetic interaction of the Mn, which has an incomplete 3d shell, present in the ordered solid solution. In the ordered state, the magnetic saturation of the $Ni_3(Fe,Mn)$ alloy is significantly greater than that of the Ni_3Fe alloy; whereas, after quenching, Mn, like other elements, lowers the magnetic saturation of the Ni_3Fe alloy (Figure 4). The additional decrease in electrical resistance during annealing is connected, for this reason, with the increase in magnetic saturation during ordering of the $Ni_3(Fe,Mn)$ alloy.

LITERATURE CITED

[1] B. G. Livshits and M. P. Ravdel, Proc. Acad. Sci. USSR, 93, No. 6 (1953).

[2] B. G. Livshits and M. P. Ravdel, Coll. Trans. TsNII Central Scientific Research Institute of Ferrous Metallurgy, No. 15, 53 (1956).

[3] F. Assmus, and F. Pfeifer, Zs. Metallkunde, 42, No. 10 (1951).

[4] F. Assmus and F. Pfeifer, Metall, 7, No. 5/6 (1953).

[5] P. Leech and C. Sykes, Phil. Mag., 27, 742 (1939).

Institute of Precision Alloys
Central Scientific Research
Institute of Ferrous Metallurgy

Received March 12, 1957

BLANK
PAGE

INVESTIGATION OF AQUEOUS SOLUTIONS OF SODIUM PARATUNGSTATE

Associate Member Acad. Sci. USSR Vikt. I. Spitsyn and G. N. Pirogova

The mechanism of the reactions occurring on acidification of solutions of normal tungstates has been comparatively little studied as yet. In the pH range of 8-6, paratungstates are formed, these being some of the most important representatives of the general class of aquopoly compounds. One of us [1] has proposed the hypothesis that an essential role in this process is played by the simultaneous presence of oxonium ions, tungstate ions, and molecules of tungstic acid, which react in solution through the formation of hydrogen bonds.

Water plays an important constitutive role in the formation of the compounds [2-4].

We have studied the properties of solutions of sodium paratungstate as they depend on conditions of formation, temperature of heating, and standing time. The methods used for this purpose were dialysis, polarography, chromatography, and light absorption.

The molecular weights of the ions present in 0.01 M tungstate solutions were determined by dialysis through a cellophane membrane at 25°. The molecular weight of the hydrated normal tungstate ion $WO_4^{2-} \cdot 2H_2O$ (M = 284) was used as a unit for comparison. A freshly prepared solution of crystalline paratungstate, $Na_{10}W_{12}O_{41} \cdot 28H_2O$, was characterized by a molecular weight of about 3000, which corresponds closely to the ion $W_{12}O_{41}^{10-} \cdot 28H_2O$ (M = 3368). After boiling the solution, the molecular weight of the anion decreased to 1500-1600, i.e., by practically half (Table 1).

TABLE 1

Dialysis Coefficients and Molecular Weights of Certain Tungstate Ions in Solution

Compound	History of the solution	pH	Dialysis coefficient, λ	Molecular weight, M
$Na_2WO_4 \cdot 2H_2O$	Freshly prepared	8.0	0.230	284
$Na_{10}W_{12}O_{41} \cdot 28H_2O$		6.1	0.072	3000
$Na_{10}W_{12}O_{41} \cdot 28H_2O$	Heated 8 hours at 100°	6.2	0.098	1600
$Na_2W_6O_{21} \cdot 10H_2O$		3.6	0.033	14000

The phenomenon which occurred can be expressed by the equation

$$Na_{10}W_{12}O_{41} \cdot 28H_2O \rightleftharpoons 2Na_5[H_2O \cdot W_6O_{21}] \cdot 12.5H_2O.$$

Evaporation leads to the formation of crystalline paratungstate which again exhibited a doubled molecular weight in solution.

Upon acidification of a solution of Na_2WO_4 with nitric acid, the composition of the anions obtained depends

TABLE 2

Change in Dialysis Coefficients and Molecular Weights of Anions During Standing of Acidified Solutions of Na_2WO_4

pH	Time of standing of solutions, days	Dialysis coefficient		Molecular weight, M	
		directly after acidification of solution	after standing of the solution	directly after acidification of solution	after standing of the solution
6.6	19	0.186	0.219	1500	1300
6.3	19	0.102	0.174	5000	1600
6.1	14	0.072	0.180	9000	1500
5.8	6	0.029	0.062	55000	14000
5.6	11	0.016	0.058	120000	14000

on the pH and the duration of the reaction (Table 2). Only in the pH range of 7.0-6.6 are hexatungstate ions formed immediately. At a pH of 6.3-6.1, ions with a molecular weight of 5000-10,000 appear first. After 10 days, the molecular weight has dropped to 1500. Apparently, in this case high molecular weight ions of the type $[H_2O \cdot W_6O_{21}]^{6-} \cdot nH_2WO_4 \cdot aq$ are formed, and these, with the passage of time, undergo disintegration, splitting off hexatungstate ions more easily. This phenomenon becomes still more apparent on further acidification. If the pH of the solution is reduced to 5.8-5.6, the molecular weight of the anions formed initially attains the enormous value of 55,000-120,000, and this decreases to only 14,000 after standing for 10 days. Sodium metatungstate, $Na_2W_4O_{13} \cdot 10H_2O$, had a similar molecular weight under the conditions of our experiments, which corresponds to approximately 12-fold polymerization of the ion $[H_2O(HWO_4)_3 \cdot (H_2WO_4)(H_2O)_4]^{2-}$ or $[W_4O_{13} \cdot 10H_2O]^{2-}$.

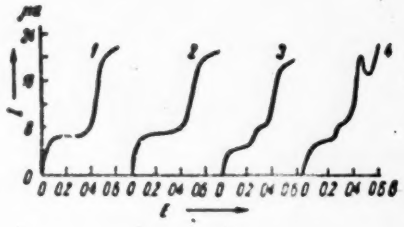


Fig. 1. Polarography with a background of 12 N HCl: 1) $2.0 \cdot 10^{-3}$ mole/liter $Na_2WO_4 \cdot 2H_2O$; 2) $1.7 \cdot 10^{-4}$ mole/liter $Na_{10}W_{12}O_{46} \cdot 28H_2O$; 3) $1.67 \cdot 10^{-4}$ mole/liter $Na_{10}W_{12}O_{46} \cdot 28H_2O$ (solution heated to boiling for 8 hours); 4) $4.18 \cdot 10^{-4}$ mole/liter $Na_2W_4O_{13} \cdot 10H_2O$. Sensitivity 1/100.

The transformations observed in solutions of tungstates were confirmed by polarography using a Heyrovsky micropolarograph. The capillary characteristic was $m^{2/3}t^{1/6} = 3.083$ mg$^{2/3}$ sec$^{1/2}$. The dropping mercury period was 2.5-2.6 seconds.

The results of the polarographic investigations are presented in Table 3 and Figure 1. It should be noted that in the strongly acid medium in which polarography of tungstate is usually carried out, colloidal tungstic or metatungstic acid, not the original tungstate ions, is present. In this regard, Na_2WO_4 and a freshly prepared solution of paratungstate behave identically (half-wave potential of -0.46 v), forming, therefore, the same product in acid medium. A solution of paratungstate which has been boiled gives still a different polarogram with two waves ($E^1_{1/2} = -0.26$ v, $E^2_{1/2} = -0.44$ v), which is more similar to polarograms of sodium metatungstate and metatungstic acid. Obviously, the hexatungstate ion is related in structure to the metatungstate ion and, perhaps, is its structural unit. The indicated conversion of paratungstate was noted polarographically, beginning at a temperature of 35° and concluding at 80°. The same difference in a freshly prepared solution of paratungstate and one which had been boiled was observed at a pH of 5.0-5.6 (acetate buffer) and against a background of K_2SO_4. It has long been known that the more acid (with respect to WO_3) the tungsten compound, the more easily it is reduced to the pentavalent state. This could explain the lower potential at the beginning of reduction (-0.26 v) of metatungstic acid (Experiments 3 and 4, Table 3) in comparison to the value obtained

for ordinary tungstic acid (Experiments 1 and 2, Table 3). However, the latter apparently appears during polarographing also in solutions of metatungstic acid, as a partial decomposition product, giving a wave with a half-wave potential of −0,44 or −0,40 v. The presence of several waves on the polarograms taken in a medium with acetate buffer and K_2SO_4 background is connected, obviously, with the presence of several forms of tungstate ions, occurring in equilibrium, which are reduced ($W^{6+} \rightarrow W^{5+}$) at different half-wave potentials. In neutral or weakly acid media, there is little probability of the occurrence of successive stages of deeper reduction of the same anion.

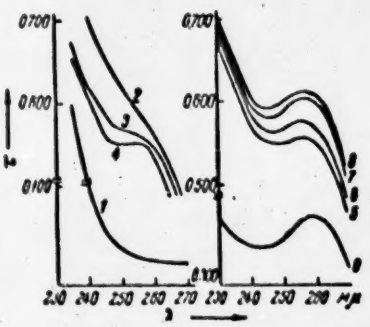


Fig. 2. Absorption spectra: 1) $2,5 \cdot 10^{-3}$ mole/liter $Na_2WO_4 \cdot 2H_2O$; 2) freshly prepared solution, $2,5 \cdot 10^{-3}$ mole/liter $Na_{10}W_{12}O_{41} \cdot 28H_2O$; 3) after 4 days; 4) after 10 days; 5) after 15 days; 6) after 18 days; 7) after 30 days; 8) after 1 year; 9) $2,5 \cdot 10^{-5}$ mole/liter $Na_2W_4O_{13} \cdot 10H_2O$.

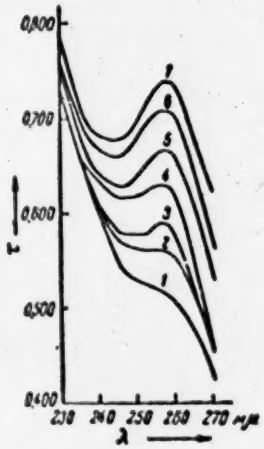


Fig. 3. Change in absorption spectra of sodium paratungstate in relation to time of boiling of the solution: 1) 1 hour; 2) 2 hours; 3) 3 hours; 4) 4 hours; 5) 6 hours; 6) 8 hours; 7) 16 hours.

The kinetics of the conversion of paratungstate ions to hexatungstate ions can also be followed by means of absorption spectra. The investigation was carried out in the ultraviolet region (220-290 mμ). Freshly prepared paratungstate solutions give curves dropping off steeply with an increase in wave length (Figure 2). On standing of the solutions, the drop in the curve in the 245-260 mμ region is suppressed, a plateau appears in this region, followed by a maximum at a wave length of 256-257 mμ. This maximum slowly increased with the course of time, and reaches a constant value a month after preparation of the solution. Subsequent observations over the course of a year disclosed no further changes in the optical properties of the solutions.

A similar, but more rapidly occurring, phenomenon takes place on heating solutions of paratungstate to boiling (Figure 3). A maximum in the 256-257 mμ region appears after three hours. Its height becomes constant after 10-16 hours boiling of the solution. Coincidence of the wave-lengths for the absorption maxima of long-standing and heated solutions confirms that the same process takes place in both cases – conversion of paratungstate ions to hexatungstate ions, to which the maximum corresponds. It is of interest to note that in this case a similarity of hexatungstate and metatungstate is observed; their absorption spectra are very closely alike (see Figure 2).

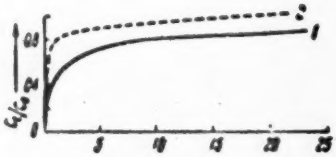
Solutions of Na_2WO_4 acidified directly after preparation give absorption spectra in the form of curves which drop off steeply with an increase in wave length. Over a period of time, a plateau appears on the curve, and then a maximum. However, this process proceeds more slowly than with solutions of sodium paratungstate.

Finally, it must be noted that freshly prepared solutions of paratungstate and solutions which have been boiled behave somewhat differently with respect to anion exchange resins. Sorption of hexatungstate ions proceeds to an appreciably lesser extent, especially at low concentrations (Figure 4).

TABLE 3

Polarography of Tungstate Solutions

Experiment No.	Compound	Concentration of sol., mol/liter	History of solution	Half-wave potential against different backgrounds		
				12 *N* HCl	CH_3COOH — CH_3COONa, pH 4.6–5.6	1 *N* K_2SO_4
1	$Na_2WO_4 \cdot 2H_2O$	10^{-3}	Freshly prepared	−0.46		
2	$Na_{10}W_{12}O_{41} \cdot 28H_2O$	10^{-4}		−0.46	−0.46 −0.92	−0.44
3	$Na_{10}W_{12}O_{41} \cdot 28H_2O$	10^{-4}	Heated to boiling 8 hours	−0.26 −0.44	−0.40 −0.90	−0.44 −0.84 −1.04
4	$Na_2W_4O_{13} \cdot 10H_2O$	10^{-4}		−0.26 −0.44	−0.40 −0.90	−0.44 −0.84 −1.04
5	$H_2W_4O_{13} \cdot 9H_2O$	10^{-4}		−0.26 −0.40	—	−0.45 −0.72 −0.98



Concentration of WO_3 mmoles/liter

Fig. 4. Absorption of paratungstate on EDE-10; anion exchange resin: 1) freshly prepared solution of $Na_{10}W_{12}O_{41} \cdot 28H_2O$; 2) solution heated to boiling 16 hours.

The similarity of the hexatungstate and metatungstate properties studied merits considerable attention. It is possible that the transition of paratungstate into hexatungstate during boiling of the solution is an important stage in the formation of metatungstates. On the other hand, the first products of the hydrolysis of metatungstates are probably hexatungstates.

LITERATURE CITED

[1] Vikt. I. Spitsyn, J. Inorg. Chem., 2, 502 (1957).

[2] A. Rosenheim, Za. anorg. Chem., 98, 157 (1916).

[3] H. Copaux, Bull. Soc. Chim. France (4), 13, 819 (1913).

[4] G. Jander and W. Heukeshoven, Za. anorg. allgem. Chem., 187, 60 (1930)

M. V. Lomonosov Moscow State University

Received March 23, 1957

SYNTHESIS OF SOME ALKYLHALOSILANES AND SILICOHYDROCARBONS

Academician A. V. Topchiev, N. S. Nametkin and T. I. Chernysheva

The present communication reports a continuation of our work studying reactions leading to formation of organosilicon compounds from unsaturated hydrocarbons and silicon compounds containing an Si–H bond [1-3]. In this work were studied reactions in which trichlorosilane and tribromosilane are added to isoamylene, 1-nonene, and 1 decene. The addition of tribromosilane was carried out under conditions similar to those used in the addition of trichlorosilane. It may be seen from Table 1 that both tribromosilane and trichlorosilane add to 1-nonene and 1-decene in the presence of benzoyl peroxide with high yields (60-70%), but they add to isoamylene only with low yields (5-8%). The decreased yields of isoamyltrichlorosilane and isoamyltribromosilane could have been due to the low reaction temperature necessitated by the low boiling point of isoamylene.

TABLE 1

Exp. No.	Formula	B.p., °C/mm Hg	Reaction Temp., °C	Reaction time, hours	Yield, %
1	i-$C_5H_{11}SiCl_3$	147.5–149/754	40	15	5.1
			100	3.5	11.7*
2	i-$C_5H_{11}SiBr_3$	196–198/751	40	15	8.5
3	$C_9H_{19}SiCl_3$	121–123/5	85	30	60.9
4	$C_9H_{19}SiBr_3$	154–157/5	85	30	79.4
5	$C_{10}H_{21}SiCl_3$	133–137/5	100	20	62.7
6	$C_{10}H_{21}SiBr_3$	167–168/5	100	20	74.0
7	$C_{18}H_{37}SiCl_3$	208–210/5	60	14	29.7
8	$C_9H_{19}SiCH_3Cl_2$	115–117/5	80	36	22.2
9	$C_{10}H_{21}SiCH_3Cl_2$	126–129/5	80	40	38

* The experiment was carried out in an autoclave under a pressure of 100 atm.

In order to exclude the effect of temperature, we carried out an experiment on the addition of trichlorosilane to isoamylene under pressure at 100° and in the presence of benzoyl peroxide. As seen from Table 1, the yield of isoamyltrichlorosilane was increased only slightly. On comparing the yields of products obtained by the addition of trichlorosilane and tribromosilane to olefinic hydrocarbons, it may be noted that the bromide is somewhat more active.

The experiments carried out by us on the addition of methyldichlorosilane to 1-nonene and 1-decene showed that this reaction gives considerably lower yields than obtained in the addition of trichlorosilane to these same hydrocarbons.

The properties of the synthesized silicohydrocarbons, obtained from the corresponding alkylhalosilanes, are given in Table 2.

TABLE 2

Exp. No.	Formula	B.p., °C/mm Hg	d_4^{20}	n_D^{20}	MR_D found	MR_D calc.
1	$i\text{-}C_5H_{11}Si(CH_3)_3$*	133–134/751	0.7295	1.4064	48.63	48.8
2	$C_4H_{11}Si(CH_3)_3$	83–85/5	0.7801	1.4321	67.32	66.52
3	$C_4H_{11}Si(CH_3)_2(C_6H_5)$	160–162/5	0.8115	1.4521	94.76	95.10
4	$C_{10}H_{21}Si(CH_3)_2(C_6H_5)$	162–164/5	0.8121	1.4529	99.13	99.73
5	$C_5H_{13}Si(C_6H_5)_3$	144–146/2	0.8053	1.4508	99.75	99.73
6	$C_9H_{19}Si(C_6H_5)_3$	167–168/5	0.8138	1.4532	108.77	108.99
7	$C_{10}H_{21}Si(C_6H_5)_3$	176–178/5	0.8139	1.4538	113.44	113.62
8	$C_{18}H_{29}Si(C_6H_5)_3$	219–223/5	0.8313	1.4669	140.17	141.40

* Literature data for $i\text{-}C_5H_{11}Si(CH_3)_3$: b.p. 131.5–132.5°/758.6 mm; d_4^{20} 0.7281; n_D^{20} 1.4057.

EXPERIMENTAL

Addition of Compounds Containing an Si–H Bond to Olefinic Hydrocarbons

1. Isoamyltribromosilane. 30 g of isoamylene (2-methyl-3-butene) and 42 g of technical tribromosilane (b.p. 108–120°) reacted in the presence of 3 g of benzoyl peroxide to give 4.4 g of isoamyltribromosilane (yield, 8.5%); b.p. 196–198°/751 mm.

Found %: Br 70.01, 70.73. $C_5H_{11}SiBr_3$. Calculated %: Br 70.79.

2. Isoamyltrichlorosilane. a) 70 g of isoamylene and 136 g of trichlorosilane reacted in the presence of 5 g of benzoyl peroxide to give 13.3 g (yield, 5.1%) of isoamyltrichlorosilane.

b) A mixture of 41.5 g of isoamylene, 81.5 g of trichlorosilane, and 2 g of benzoyl peroxide were heated in an autoclave at 100° and 100 atm. pressure; 13.6 g (yield 11.14%) of isoamyltrichlorosilane was obtained; b.p. 147°/754 mm.

Found %: Cl 52.15, 51.56. $C_5H_{11}SiCl_3$. Calculated %: Cl 51.77.

3. Nonyltribromosilane. From 15 g of 1-nonene, 32 g of technical tribromosilane (b.p. 110–120°), and 4 g of benzoyl peroxide was obtained 36 g (yield, 79.4%) of nonyltribromosilane; b.p. 154–157°/5 mm; d_4^{20} 1.4500; n_D^{20} 1.4764; MR_D 76.40, calc. 75.21.

Found %: Br 59.91, 60.22. $C_9H_{19}SiBr_3$. Calculated %: Br 60.78.

4. Nonyltrichlorosilane. From 84 g of 1-nonene, 90 g of trichlorosilane, and 5 g of benzoyl peroxide was obtained 106 g (yield, 60.99%) of nonyltrichlorosilane; b.p. 121–123°/5 mm; d_4^{20} 1.0645; n_D^{20} 1.4498; MR_D 66.05, calc. 66.25.

Found %: Cl 40.42, 40.46. $C_9H_{19}SiCl_3$. Calculated %: Cl 40.72.

5. Decyltribromosilane. From 17 g of 1-decene, 30 g of technical tribromosilane, and 3 g of benzoyl peroxide was obtained 33 g (yield, 74%) of decyltribromosilane; b.p. 166–169°/5 mm; d_4^{20} 1.3896; n_D^{20} 1.4692; MR_D 80.27, calc. 79.84.

Found %: Br 57.94, 58.78. $C_{10}H_{21}SiBr_3$. Calculated %: Br 58.69.

6. Decyltrichlorosilane. From 80 g of 1-decene, 80 g of trichlorosilane, and 5 g of benzoyl peroxide was obtained 92 g (yield, 62.7%) of decyltrichlorosilane; b.p. 137°/10 mm; d_4^{20} 1.0540; n_D^{20} 1.4528; MR_D 70.95; calc. 70.84.

Found %: Cl 38.81, 38.41. $C_{10}H_{21}SiCl_3$. Calculated %: Cl 38.66.

Literature data [4] for $C_{10}H_{21}SiCl_3$: b.p. 189°/84 mm.

7. Hexadecyltrichlorosilane. From 28.7 g of 1-hexadecene, 93 g of trichlorosilane, and 5 g of benzoyl peroxide was obtained 13.3 g (yield, 29.7%) of hexadecyltrichlorosilane; b.p. 208°/5 mm.

Found %: Cl 29.52, 29.64. $C_{16}H_{33}SiCl_3$. Calculated %: Cl 29.62.

Literature data [5] for $C_{16}H_{33}SiCl_3$: b.p. 194-196°/7.5 mm.

8. Nonylmethyldichlorosilane. From 21 g of 1-nonene, 110 g of methyldichlorosilane, and 5 g of benzoyl peroxide was obtained 8.5 g (yield, 21.2%) of nonylmethyldichlorosilane; b.p. 115-117°/5mm; d_4^{20} 0.9931; n_D^{20} 1.4548; MR_D 65.91, calc. 66.58.

Found %: Cl 28.47, 28.55. $C_{10}H_{22}SiCl_2$. Calculated %: Cl 29.21.

9. Decylmethyldichlorosilane. From 24 g of 1-decene, 100 g of methyldichlorosilane, and 5 g of benzoyl peroxide was obtained 15.7 g (yield, 38%) of decylmethyldichlorosilane; b.p. 126-129°/5 mm; d_4^{20} 0.9859; n_D^{20} 1.4542; MR_D 70.17, calc. 71.21.

Found %: Cl 27.75, 27.82. $C_{11}H_{24}SiCl_2$. Calculated %: Cl 27.84.

Preparation of Silicohydrocarbons

Silicohydrocarbons were prepared with the aid of organolithium compounds. To the previously prepared ethereal solution of organolithium compound was added the halogen derivative of an organosilicon compound. The mixture was heated at the boiling point of ether for 10 hours. The resulting silicohydrocarbon was treated by extraction with concentrated sulfuric acid and distilled over metallic sodium. The basic properties of the silicohydrocarbons prepared by us are presented in Table 2.

1. Isoamyltrimethylsilane. From 7 g of lithium, 70 g of methyl iodide, and 18 g of isoamyltrichlorosilane was obtained 11.7 g (yield, 96.3%) of isoamyltrimethylsilane; b.p. 133-134°/751 mm;

Found %: C 66.64, 66.61; H 14.04, 13.98. $C_8H_{20}Si$. Calculated %: C 66.58; H 13.37.

2. Nonyltrimethylsilane. From 4.5 g of lithium, 45 g of methyl iodide, and 16 g of nonyltribromosilane was obtained 7.2 g (yield, 68.8%) of nonyltrimethylsilane; b.p. 83-85°/5 mm;

Found %: C 72.54, 72.59; H 13.92, 13.82. $C_{12}H_{28}Si$. Calculated %: C 71.91; H 14.08.

3. Nonylmethyldibutylsilane. Fom 6 g of lithium, 55 g of butyl bromide, and 5 g of nonylmethyldichlorosilane was obtained 4.2 g (yield, 71.2%) of nonylmethyldibutylsilane; b.p. 160-162°/5 mm;

Found %: C 76.88, 76.85; H 13.89, 13.87. $C_{18}H_{40}Si$. Calculated %: C 75.98; H 14.17.

4. Decylmethyldibutylsilane. From 4 g of lithium, 50 g of butyl bromide, and 7 g of decylmethyldichlorosilane was obtained 5.2 g (yield, 63.4%) of decylmethyldibutylsilane; b.p. 162-164°/5 mm;

Found %: C 76.47; 76.30; H 14.02, 14.07. $C_{19}H_{42}Si$. Calculated %: C 76.42; H 14.18.

5. Heptyltributylsilane. From 14 g of lithium, 140 g of butyl bromide, and 74 g of heptyltribromosilane was obtained 42 g (yield, 70%) of heptyltributylsilane; b.p. 144-146°/2 mm;

Found %: C 76.22; 76.24; H 14.16, 14.17. $C_{19}H_{42}Si$. Calculated %: C 76.42; H 14.18.

6. Nonyltributylsilane. From 15 g of lithium, 140 g of butyl bromide, and 50 g of nonyltrichlorosilane was obtained 42.4 g (yield, 68%) of nonyltributylsilane; b.p. 167-168°/5 mm;

Found %: C 77.06, 77.10; H 14.46, 14.32. $C_{21}H_{46}Si$. Calculated %: C 77.22; H 14.37.

7. Decyltributylsilane. From 9 g of lithium, 90 g of butyl bromide, and 30 g of decyltrichlorosilane was obtained 25.7 g (yield, 67%) of decyltributylsilane; b.p. 176-178°/5 mm.

Found %: C 77.59, 77.56; H 13.94, 14.01. $C_{22}H_{48}Si$. Calculated %: C 77.56; H 14.20.

8. Hexadecyltributylsilane. From 4 g of lithium, 42 g of butyl bromide, and 9 g of hexadecyltrichlorosilane was obtained 6.4 g (yield, 60.4%) of hexadecyltributylsilane; b.p. 219-223°/5 mm.

Found %: C 79.03, 78.95; H 14.09, 14.12. $C_{28}H_{60}Si$. Calculated %: C 79.24; H 14.15.

LITERATURE CITED

[1] A. V. Topchiev, N. S. Nametkin and O. P. Solovova, Proc. Acad. Sci. USSR, 86, No. 5, 965 (1952).

[2] N. S. Nametkin, A. P. Topchiev and O. P. Solovova, Proc. Acad. Sci. USSR, 93, No. 2, 285 (1953).

[3] A. V. Topchiev, N. S. Nametkin, T. L. Chemysheva and S. G. Dugaryan, Proc. Acad. Sci. USSR, 110, No. 1 (1956).*

[4] F. Whitmore and L. Sommer, et al., Am. J. Chem. Soc., 68, 475 (1946).

[5] A. Barry, L. DePree, J. Gilkey and D. Hook, J. Am. Chem. Soc., 69, 2918 (1947).

Received May 18, 1956

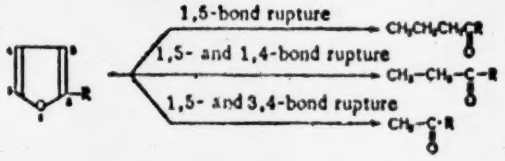
* Original Russian pagination. See C. B. Translation.

CATALYTIC HYDROGENOLYSIS OF SYLVAN OVER VARIOUS CATALYSTS

Associate Member Acad. Sci. USSR N. I. Shuikin and I. F. Belsky

The reactions occurring during the hydrogenolysis of furan homologs depends on three factors: process conditions, nature of the catalyst, and temperature. During hydrogenation of sylvan in the liquid phase over copper-chromium oxide, the furan ring cleaves almost equally at the 1,2- and 1,5-ether bonds, which results in the formation of, respectively, 1-pentanol and 2-pentanol [1]. In contrast to this, hydrogenolysis of sylvan in the liquid phase over Adams platinum catalyst results in cleavage of only the 1,5-C–O bond [2]. Hydrogenolysis of sylvan in the vapor phase over nickel [3] and copper [4] catalysts also occurs at the 1,5-C–O bond, but the product of the reaction in this case is not an alcohol, but a ketone (2-pentanone).

We have investigated the hydrogenolysis of furan homologs in the vapor phase over skeletal nickel-aluminum catalyst, and it was shown that over this catalyst hydrogenolysis takes place not only at the ether, but also at carbon-carbon bonds in the furan ring [5-7]. All furan homologs having an alkyl or alkenyl substituent in the α-position undergo hydrogenolysis in three directions:



(I)
(II)
(III)

At 175° and lower, the furan ring undergoes hydrogenolysis only in directions (I) and (II), but at higher temperatures (235°) it also proceeds in direction (III). In the present article, we present the results of an investigation of the hydrogenolysis of sylvan in the presence of various catalysts: platinum on carbon (15% Pt), palladium on carbon (10% Pd), Adkins copper-chromium oxide, nickel on aluminum oxide (30% Ni), and skeletal nickel-aluminum catalyst.

This last was prepared by leaching 10-15% of the aluminum from a Ni-Al alloy containing 27% Ni. The reaction was carried out in a flow-type apparatus in the vapor phase at 275°. The sylvan space rate was 0.1 hours^{-1}. The products were fractionated in a column with 30 theoretical plates, and were then identified by determination of the physical constants and by conversion of the ketones formed to the semicarbazones.

Hydrogenolysis of sylvan over skeletal Ni-Al catalyst. By passing 120 g of sylvan over Ni-Al catalyst in a stream of hydrogen at 275°, 92 g of catalyzate was obtained, from which the following compounds were isolated:

1. Acetone (35%). Semicarbazone, m.p. 186°.
2. Methyl ethyl ketone (24%), b.p. 78.5-79.5° (743 mm), d_4^{19} 0.8068, n_D^{19} 1.3796. Semicarbazone, m.p. 146-147°.
3. Methyl propyl ketone (36%), b.p. 100.5-001° (743 mm), d_4^{19} 0.8071, n_D^{19} 1.3912. Semicarbazone, m.p. 110°.

The higher boiling fraction of the catalyzate (amounting to about 5%) was not investigated. The gaseous reaction products, after separation from hydrogen, were analyzed chromatographically. The composition was methane (3%), ethane (64%), propane (22%), and butane (11%).

Hydrogenolysis of sylvan over Ni-Al_2O_3 catalyst. Hydrogenation at 275° of 100 g of sylvan gave 67 g of catalyzate and 16 g of water. Unconverted sylvan (36%), n-pentane (10%), and methyl propyl ketone (9%) were isolated in the pure state from the catalyzate.

A fraction boiling at 77-80° (753 mm), n_D^{20} 1.3930, which amounted to 8%, gave a semicarbazone with a m.p. of 147°, which indicates the presence of methyl ethyl ketone in the fraction. After treatment of this fraction with sodium bisulfite, pure tetrahydrosylvan was obtained.

A large part (37%) of the catalyzate boiled in the range of 60-150° (8 mm); it was not investigated further. It was probably a mixture of glycols and condensation products.

120 g of sylvan was subjected to hydrogenation at 400°. This gave 78 g of catalyzate and 16 g of water. The catalyzate contained unconverted sylvan (24%), n-pentane (8%), acetone (10%), methyl ethyl ketone (6%), tetrahydrosylvan (6%), methyl propyl ketone (6%), and higher boiling residue (40%).

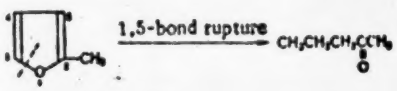
Hydrogenation of sylvan over copper-chromium oxide. The copper-chromium catalyst was only slightly active for the hydrogenation of sylvan in the vapor phase at 275°. After a single pass of the sylvan over the catalyst, about 80% of the sylvan was unreacted. The reaction products consisted of 2-pentanone (75% yield, calculated on the sylvan converted and a residue boiling above 150°.

Hydrogenation of sylvan over platinized carbon. In a single pass over the platinum catalyst at 275°, 120 g of sylvan gave 116 g of a catalyzate containing 2-pentanone (85%) and unconverted sylvan (15%).

Hydrogenolysis of sylvan over palladinized carbon. Hydrogenation of 120 g sylvan at 275° over palladium deposited on activated carbon gave 118 g of a catalyzate consisting of tetrahydrosylvan (71%) and 2-pentanone (29%).

The results of the present investigation lead to the conclusion that the direction and depth of the hydrogenolysis of the furan ring depends essentially on the nature of the catalyst.

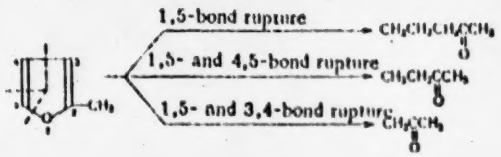
Platinum deposited on carbon is selective for the hydrogenolysis of the ring in sylvan only at the 1,5-ether bond.



The exclusive presence of 2-pentanone and unconverted sylvan in the reaction products shows that at 275° over platinum catalyst, the hydrogenolysis reaction proceeds at an incomparably higher rate than does hydrogenation of the double bonds in the ring. 2-Pentanone is formed in practically quantitative yield calculated on the reacting sylvan. On the other hand, palladium catalyst is effective in the hydrogenation of the double bonds in the ring, but displays only a low activity with respect to hydrogenolysis of the ether bond. As in the case of platinum, in the presence of palladium the furan ring undergoes hydrogenolysis only at the 1,5-bond, which results in the formation of 2-pentanone. At 275°, the copper-chromium catalyst displays very high activity for both hydrogenation and hydrogenolysis of the furan ring. In contrast to the hydrogenolysis of sylvan in the liquid phase over copper-chromium oxide, which leads to the formation of two alcohols [1], the vapor-phase reaction over this catalyst proceeds only with the rupture of the ether bond not adjoining the side chain.

There is a wide difference between skeletal nickel-aluminum catalyst and nickel on aluminum oxide with respect to their ability to promote hydrogenolysis of the furan ring. Over nickel-alumina catalyst at 275°, only about 15% ketones is formed; 85% of the catalyzate consists of unconverted sylvan, n-pentane, and high boiling compounds. This shows that nickel on aluminum oxide promotes processes involving deep decomposition of the furan ring and the formation of molecules having a more complex composition.

Over skeletal nickel-aluminum catalyst, the furan ring undergoes hydrogenolysis in three directions:



These results are in agreement with our previous observations [5-7] on the hydrogenolysis of higher furan homologs over skeletal nickel-aluminum catalyst. Thus, of all the catalysts investigated only skeletal nickel-aluminum catalyst has the ability to promote smoothly the hydrogenolysis of the furan ring both in the direction of cleavage of the 1,5-ether bond and in the direction of paired cleavage of the 1,5- and 4,5- and of the 1,5- and 3,4-bonds. This property of the catalyst presents the practical possibility of the production of aliphatic ketones of different structures through hydrogenolysis of alkyl furans.

LITERATURE CITED

[1] R. Connor and H. Adkins, J. Am. Chem. Soc., 54, 4687 (1932).

[2] H. Smith and J. Fuzek, J. Am. Chem. Soc., 71, 415 (1949).

[3] C. Wilson, J. Am. Chem. Soc., 70, 1313 (1948).

[4] J. Bremmer, D. Jones and R. Coats, Brit. Pat. 63408 (1950); Chem. Abstr., 44, 7884 (1950).

[5] N. I. Shuikin, V. A. Tulupov and I. F. Belsky, J. Gen. Chem., 25, 1175 (1955).

[6] N. I. Shuikin and I. F. Belsky, J. Gen. Chem., 26, 2716 (1956).

[7] N. I. Shuikin and I. F. Belsky, Bull. Soc. Chim., 1956, 1556.

N. D. Zelinsky Institute
of Organic Chemistry
Academy of Sciences USSR

Received March 27, 1957

BLANK
PAGE

THE BINDING OF LIME IN CALCIUM HYDROSILICATE UNDER NORMAL CONDITIONS

V. F. Abrosenkova, G. I. Loginov and Academician P. A. Rebinder

It is generally assumed that the formation of calcium hydrosilicate when lime is reacted with silica in water medium can be realized in the hardening of lime-silica cements for construction materials only under the conditions of hydrothermal treatment in autoclaves at temperatures of the order of 170°. It was believed that this process fails to go at ordinary temperatures, i.e., it does not appear in a noticeable increase in the strength of the shaped article.

A study of these processes has been the subject of quite a few papers, dealing with the technological schemes for the production of silicate brick, tile and a series of construction items [1]. However, some construction materials like, for example, wall blocks, finding constantly expanding use in the construction of low-storied buildings, do not require the high strength that can be obtained with the autoclave treatment.

On the other hand, the studies made by us to develop the physicochemical principles underlying the technology of manufacturing wall construction blocks [2] give basis to assume that, together with hydrational hardening [3,4] of the lime-sand cement, there is also gradual binding of the calcium hydrosilicate in the surface layers of the grains of sand. The greater the surface area of the sand grain and the stronger its activation during the process of mutual grinding with lime, the greater was the amount of lime bound in the calcium hydrosilicate.

By means of the radioactive Ca^{45} isotope, used as the hydroxide $Ca^{45}(OH)_2$, it was established on coarse-grained sands that the amount of bound calcium is proportional to the specific surface of the sand [5]. In the first stage the binding of the calcium bears an irreversible adsorption character, migrating into a surface chemical reaction.

This same method was used in the indicated paper to study the kinetics for the slow binding of calcium from a saturated solution by sand with a more highly developed specific surface (up to 2.9 sq. m./g.). For this purpose a method for the determination of calcium was developed, which excluded the influence of carbon dioxide from either the water or the atmosphere. The amount of bound calcium was determined by the difference in the activities of the original calcium hydroxide solution and the same solution after the lime had been allowed to react with the sand for a given length of time.

In accord with the character of the kinetics curves shown in Fig. 1 the process for the binding of lime in calcium hydrosilicate at room temperature consists of two stages: irreversible binding in the surface layer of the sand grains during the early days and then a diffusion process, proceeding at a constant rate.

Actually, if the area is calculated, corresponding to a monomolecular covering of the calcium hydrosilicate for transition to a constant binding rate, then the amount of lime, bound by 1 sq. mm. of the sand grain surface, in such a covering proves to be constant (Fig. 1). This calculation leads to $S_0 = 6\text{Å}^2/\text{Ca ion}$. The next stage for the reaction of lime with sand bears the character of a diffusion process.

When finely ground sand, activated during the process of its mutual grinding with the lime, is added to the cement composition, the strength of the articles, prepared on this binder with a sand (unground) filler, shows a constant increase with time. Increase in strength of these articles under natural conditions is determined by the concurrent processes of binding the lime in the calcium hydrosilicate by silica and in the calcium

carbonate by carbon dioxide. The indicated processes proceed very slowly, since the diffusion process lies at the base of both processes.

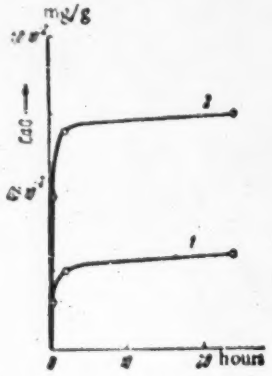


Fig. 1. Kinetics of the binding of calcium oxide by sand: 1) not ground, with a specific surface of 150 sq. cm./g; 2) ground, with a specific surface of 500 sq. cm./g.

TABLE 2

Batch composition, %				Strength limit, kg/cm²					
binder		unground sand	mixing water	7 days	1 month	3 months	6 months	1 year	2 years
lime	sand								
12.5	12.5	75 (coarse)	7.5	20	28	—	—	49	—
10	10	80 (medium grainy)	8	12	20	28	36	—	48

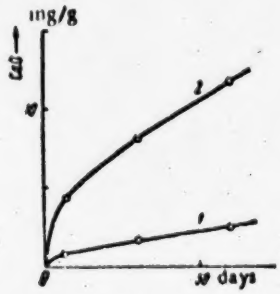


Fig. 2. Kinetics of the binding of calcium oxide by finely ground sand with specific surface: 1) 0.7 sq. m./g.; 2) 2.9 sq. m./g.

TABLE 1

Specific surface S, sq. m./g.	Amount of CaO, bound with a full cover a, mg./g.	Adsorption a/S = = G mg./sq. m.
0.015	0.025	1.6
0.05	0.07	1.4
0.15	0.25	1.6
0.7	1.0	1.4
2.9	4.5	1.5

Thus, for hollow blocks with dimensions 390 x 190 x 190 cu. mm., prepared on a 1:1 lime-sand binder from unslaked lime, ground together with sand to an effective specific surface of 1.25 sq. m./g., the resistance to compression shows a constant increase. Small amounts (0.2-0.4% on the weight of lime) of substances, functioning as plasticizers and as retarders of the hydrational hardening, were added to the mixing water (Table 2).

For the data given in Table 2 we took the average values from many portions of the blocks, prepared by the technology that had been worked out together with the All-Union Scientific-Research Institute of New Problems on the Fine Grinding of Construction Materials by the Vibro Principle (VNIITISM).

Sufficient basis exists to assume that the carbonation of calcium hydroxide proceeds at a much slower rate than does its silicatization. In part, this is confirmed by the x-ray structure analysis data: when kept under ordinary conditions the line, characteristic for calcium monohydrosilicate and corresponding to an interplanar distance of 3.01 Å [6], appears on the x-ray pattern only after the lapse of 2 years, while the line, corresponding to calcium carbonate, is absent.

LITERATURE CITED

[1] P. P. Budnikov and L. G. Gulinova, Colloid J. (USSR), No. 3, 195 (1937); Yu. M. Butt and L. L. Rashkovich, Suppl. Transactions ROSNIIMS, No. 10 (1956).

[2] G. L. Logginov, N. E. Levina and V. F. Abrosenkova, Informational Communications of the VNIITISM, No. 6 (1956).

[3] B. V. Osin, Unslaked Lime, 1954.

[4] G. L. Logginov, P. A. Rebinder and V. P. Sukhova, Proc. Acad. Sci. USSR, 99, No. 4 (1954).

[5] G. L. Logginov, Trans. Conference on the Use of Vibrogrinding in the Industry of Construction Materials, 1957.

[6] R. H. Bogue, Magazine of Concrete Research, December, No. 14, 90 (1953); H. F. McMurdie and E. P. Flint, J. Res. Nat. Bur. Stand., 31, 225 (1943).

Institute of Physical Chemistry
Academy of Sciences of the USSR

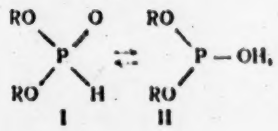
Received April 6, 1957

BLANK
PAGE

TAUTOMERISM OF DIPHENYL PHOSPHITE

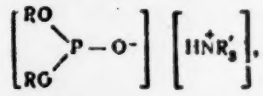
Acad. Sci. USSR Correspondent Member M. I. Kabachnik and Yu. M. Polikarpov

The tautomerism of the dialkyl phosphites

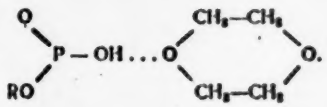


I II

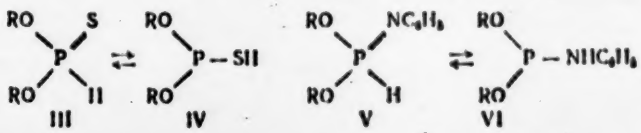
discovered by A. E. Arbuzov [1] and Milobendzki [2], has been the subject of numerous investigations. On the basis of studying the chemical properties and the spectroscopic and refractometric data it can be considered established that the position of the equilibrium for this tautomeric system is strongly shifted toward form I. The dialkyl phosphites in the free state do not show the properties characteristic for trivalent phosphorus compounds, and in particular they do not react in the sense of addition involving the free electron pair on the phosphorus atom in form II. In solutions the dialkyl phosphites also do not show a capacity for addition reactions, except with strongly basic compounds, such as the tertiary amines. In these solutions, together with undissociated dialkyl phosphite molecules, salts of the type



are present, the anion of which easily adds sulfur [3] and phenyl azide [4]. It was shown by M. I. Kabachnik and E. I. Golubeva [5] that the dialkyl phosphites add sulfur with comparative ease also in dioxane medium, in which form II can be stabilized by the stable hydrogen bond



All of these data indicate that the equilibrium of the dialkyl phosphites is shifted toward form I, and the action of definite external factors is necessary to enable the system to show the properties of a trivalent phosphorus compound. If we proceed from the representations, developed by one of us [6], and regard the tautomeric equilibrium shown by the dialkyl phosphites as being an acid-base protolytic equilibrium, shifted toward the



III IV V VI

less acid form I, then in the transition to analogs of the dialkyl phosphites it is possible, by changing the structure of the molecule in suitable manner, to change the ratio of the acidity constants of the forms and in that way obtain systems with a different position of the tautomeric equilibrium. Thus, the equilibrium of the dialkyl thiophosphites, as was shown by M. I. Kabachnik and T. A. Mastryukova [7], is strongly shifted toward form III, in which connection there is basis to assume that it is shifted to an even greater degree than for the dialkyl phosphites, while the tautomeric equilibrium of the dialkyl anilidophosphites, studied by M. I. Kabachnik and V. A. Gilyarov [8], is already shifted toward form VI. Such a difference in the tautomeric ratios is explained by a decrease in the ionizability of the bonds in the series SH>OH>NH. In the presented two examples a change in the position of the tautomeric equilibrium was achieved by a very substantial change in the composition of the diad system.

Our problem was to find a similar type of effect with retention of the diad system of H-P=O bonds, characteristic for the dialkyl phosphites. This could be expected if the alkoxy groups of dialkyl phosphites were replaced by more electrophilic groups, the influence of which would be to raise the acid properties of form I. We chose diphenyl phosphite as an example of this. If the above considerations are correct then diphenyl phosphite, in contrast to the dialkyl phosphites, should be characterized by showing the typical reactions of addition to the unshared pair of electrons of trivalent phosphorus.

Two literature references exist on the synthesis of diphenyl phosphite [9,10]. The chemical properties of diphenyl phosphite have not been studied.

We obtained diphenyl phosphite in quantitative yield by the careful saponification of diphenyl chlorophosphite in ether with an equivalent amount of water, followed by removal of the hydrogen chloride and solvent in vacuo:

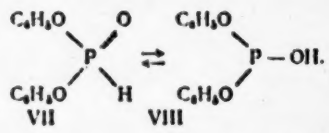
$$(C_6H_5O)_2PCl + H_2O \rightarrow (C_6H_5O)_2POH + HCl.$$

B.p. 100-101° at $3 \cdot 10^{-4}$ mm, n_D^{20} 1.5590, d_4^{20} 1.2318. MR_D found 61.37.

Found %: C 61.39; 61.53; H 4.35; 4.47; P 13.20, 12.97. $C_{12}H_{11}O_3P$. Calculated %: C 61.54; H 4.73; P 13.23.

The infrared spectrum of diphenyl phosphite shows distinct absorption bands, indicating the presence of P-H (2420 cm^{-1}) and P=O (1280 cm^{-1}) bonds in the molecule; a noticeable absorption failed to be observed in the region characteristic for the hydroxyl group (Fig. 1). As a result, the spectroscopic data speak in favor of a diphenyl phosphite structure with a pentavalentphosphorus atom; a comparison of the found molecular refraction (61.37) with the values, calculated for each of the structures separately (calculated MR_D for VII = 61.46, and for VIII = 63.37), leads to the same conclusion.

However, the chemical properties of diphenyl phosphite very definitely testify to the presence of a substantial amount of form VIII in equilibrium with form VII:

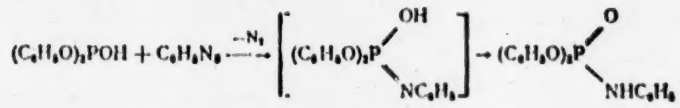


VII VIII

We found that diphenyl phosphite enters into the following characteristic reactions of addition to the free electron pair of trivalent phosphorus.

Addition of Phenyl Azide. It is known that trialkyl- and triarylphosphines add phenyl azide with the formation of phosphinimines. M. I. Kabachnik and V. A. Gilyarov extended this reaction to the full esters of trivalent phosphorus acids; the dialkyl phosphites do not react with phenyl azide [12].

We found that diphenyl phosphite already reacts in the cold with phenyl azide to give diphenyl anilidophosphate:



A mixture of equimolar amounts of diphenyl phosphite and phenyl azide was allowed to stand in a sealed ampul in the dark at room temperature for 4 months. The yield of diphenyl anilidophosphate was 25%, m.p. 128-129° (from aqueous alcohol), the mixed m.p. with the authentic substance, obtained from diphenyl chlorophosphate and aniline, was not depressed. From the literature [13], m.p. 129-130°. When heated the reaction proceeds much more rapidly and with a better yield (in 3 hours at 100°—50%).

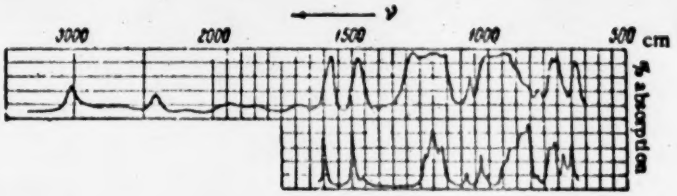
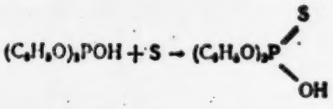


Fig. 1. Infrared spectrum of diphenyl phosphite (for comparison the spectrum of triphenyl phosphite [11] is given at the bottom).

Addition of Sulfur. In the absence of solvent and base the dialkyl phosphites do not add sulfur. In contrast to them, diphenyl phosphite reacts with sulfur when equimolar amounts of the two reactants are heated in the absence of a solvent



The sulfur reacts to the extent of 77% in 8 hours at 120°. The diphenyl thiophosphate, together with unreacted diphenyl phosphite, was isolated by treating an ether solution of the reaction mixture with aqueous alkali and subsequent acidification with hydrochloric acid. Diphenyl thiophosphate was characterized as the cyclohexylammonium salt—colorless needles (from aqueous alcohol), yield 26% (calculated on the basis of reacted sulfur), m.p. 127-129°. From the literature [14], m.p. 127-128°.

Found %: C 59.29, 59.37; H 6.63, 6.76; P 8.45, 8.42; S 8.58, 8.38; N 3.76, 3.73. $C_{18}H_{26}O_3PSN$. Calculated %: C 59.16; H 6.62; P 8.48; S 8.76; N 3.83.

The addition of sulfur under the indicated conditions is accompanied by hydrogen sulfide evolution, and together with the diphenyl thiophosphate, a substantial amount of triphenyl thiophosphate was isolated from the reaction mixture.

Addition of Cuprous Chloride. The reaction with copper monohalides, leading to the formation of crystal-

line complexes, was proposed by A. E. Arbuzov [1] as being characteristic for trivalent phosphorus compounds. It was specifically on the basis of the dialkyl phosphites failing to show this reaction that A. E. Arbuzov concluded that the phosphorus atom in them was pentavalent.

We found that cuprous chloride dissolves in diphenyl phosphite with the formation of a crystalline complex having the composition $(C_6H_5O)_2POH \cdot CuCl$.

After short heating of equimolar amounts of the reactants, followed by solution of the reaction mixture in ether and removal of most of the unreacted cuprous chloride, the complex was precipitated with methyl alcohol, and then reprecipitated from dioxane with petroleum ether. White powder, decomposing when heated to ~120°.

Found %: C 43.27, 43.52; H 3.22, 3.19; Cl 10.67, 10.87. $C_{12}H_{11}O_3PCuCl$. Calculated %: C 43.28; H 3.33; Cl 10.64; Ash 45.17. Found Ash 44.61, 44.88.

Reaction of Diphenyl Phosphite with Diazomethane. In contrast to the dialkyl phosphites, diphenyl phosphite, being more acidic, reacts with diazomethane in ether solution with the liberation of nitrogen:

$$(C_6H_5O)_2POH + CH_2N_2 \rightarrow (C_6H_5O)_2POCH_3 + N_2$$

Removal of the excess diazomethane with the solvent, followed by vacuum-fractionation, gave diphenyl methyl phosphite. Yield 58%, b.p. 101-103°/2 mm, n_D^{20} 1.5575, d_4^{20} 1.1663, MR_D found 68-56, calculated 68-10. From the literature [15], b.p. 165.5-166.5°/12 mm, n_D^{25} 1.5528, d_4^{25} 1.1644.

Found %: C 62.88, 62.82; H 5.36, 5.35; P 12.11, 12.11. $C_{13}H_{13}O_3P$. Calculated %: C 62.90; H 5.28; P 12.48.

The obtained diphenylmethyl phosphite was dissolved with heating in cuprous chloride; after two precipitations from ether with methyl alcohol the complex $(C_6H_5O)_2POCH_3 \cdot CuCl$ was obtained in nearly quantitative yield, being a very viscous clear colorless sirup, which we were unable to crystallize.

Found %: C 45.57, 45.44; H 3.77, 3.74; Cl 10.20, 10.38; Ash 43.00, 42.84. $C_{13}H_{13}O_3PCuCl$. Calculated %: C 44.97; H 3.77; Cl 10.21; Ash 43.35.

The addition of diazomethane to yield the full phosphorous acid ester can be regarded as still further proof (within the scope of the rigid criteria of Arndt [15]) of the presence of the tautomeric form with trivalent phosphorus in the diphenyl phosphite equilibrium system. Here, in contrast to the previous addition reactions involving the free electron pair of the phosphorus, this form was shown by a reaction involving the hydroxyl group.

LITERATURE CITED

[1] A. E. Arbuzov, "The Structure of Phosphorus Acid and Its Derivatives," Dissertation, St. Petersburg, 1906, Selected Works, p. 41 (1952), Acad. Sci. USSR Press; A. E. Arbuzov, Trans. Session Acad. Sci. USSR on Organic Chemistry, 1938.

[2] T. Milobendzki, Ber., 45, 298 (1912).

[3] A. E. Arbuzov, Collection Abstracts of the Sixth Mendeleev Convention, Part II, p. 124 (1932), Kharkov; O. Foss, Acta Chem. Scand., 1, 12 (1947).

[4] V. A. Gilyarov, Trans. Conference on the Chemistry and Application of Organophosphorus Compounds, Kazan, 1955, p. 215 (1957), Acad. Sci. USSR Press.

[5] M. I. Kabachnik and E. I. Golubeva, Proc. Acad. Sci. USSR, 105, 1258 (1955).

[6] M. I. Kabachnik, Proc. Acad. Sci. USSR, 83, 407 (1952); 83, 859 (1952).

[7] M. I. Kabachnik and T. A. Mastryukova, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1953, 163.*

* Original Russian pagination. See C. B. Translation.

[8] M. I. Kabachnik and V. A. Gilyarov, Proc. Acad. Sci. USSR, 96, 991 (1954).

[9] E. Noack, Lieb. Ann., 218, 92 (1883).

[10] T. Milobendzki and K. Szulgin, Chemik Polski, 15, 66 (1917).

[11] L. Bellamy and L. Beecher, J. Chem. Soc., 1952, 475.

[12] M. I. Kabachnik and V. A. Gilyarov, Proc. Acad. Sci. USSR, 106, 473 (1956); Bull. Acad. Sci. USSR, Div. Chem. Sci., 1956, 790.*

[13] L. Audrieth and A. Toy, J. Am. Chem. Soc., 64, 1337 (1942).

[14] J. Lecocq and A. R. Todd, J. Chem. Soc. 1954, 2381.

[15] A. E. Arbuzov and I. V. Nesterov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, 427.*

[16] F. Arndt, Rev. Fac. Sci. Univ. Istanbul. 1, No. 4, 1 (1936).

Institute of Organoelement Compounds
Academy of Sciences of the USSR

Received March 22, 1957

* Original Russian Translation. See C. B. Translation.

BLANK
PAGE

COMPLEX FORMATION AND CHAIN STRUCTURE IN THE POLYMERIZATION OF DIVINYL WITH BUTYLLITHIUM

V. A. Kropachev, B. A. Dolgoplosk and N. I. Nikolaev

(Presented by Academician V. A. Kargin, February 27, 1957)

It was established in a number of studies [1-3] that the chain structure in the catalytic polymerization of monoolefins and dienes is determined to a large degree by the nature of the catalytic complex, participating in the polymerization process. At the same time it was shown that the initial catalytic complex bears a direct relationship to each elementary act of the chain growth.

The isolation of organolithium compounds in the pure state is associated with great experimental difficulties. Together with the formation of the organometal compounds the possibility of a complex mixture of their oxidation products being formed is not excluded. To elucidate the influence of the indicated oxidation products on the chain structure in the polymerization of butadiene it seemed expedient to investigate the influence of oxygen.

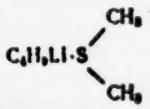
As the result of the investigation made by us it was established that in the polymerization of divinyl with organolithium compounds the introduction of comparatively small amounts of oxygen into the system leads to a substantial increase in the number of 1,2 links in the polybutadiene at the expense of a reduction in the number of 1,4 links. The addition of either alcohol or phenol exerts a similar influence on the structure of the polymeric chain (Table 1).

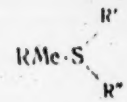
In principle the obtained results are of interest in the sense that they show the need for protecting the system from the entrance of oxygen when the problem is to synthesize divinyl polymers with the maximum amount of 1,4 links in the chain. The influence of oxygen on the polybutadiene structure is apparently due to the formation of oxygen-containing products, which form complexes with organolithium compounds.

A similar effect is shown by the dialkyl monosulfides, the influence of which was studied by us in detail. The effect of adding dimethyl, dipropyl and diisopropyl sulfides on the structure of the polybutadiene chain when the polymerization was done in the absence of oxygen was studied.

The experimental data, obtained when butadiene was polymerized with butyllithium in the presence of dialkyl sulfides, revealed that the latter substantially increase the amount of 1,2 links in the chain. In the case of dimethylsulfide the amount of 1,2 links is increased from 12 to 68% (Table 2).

From the data given in Table 2 it can be seen that the influence of the dialkyl sulfide decreases with increase in the size of the alkyl radical. Earlier [4] we had shown on the example of butyllithium the ability of organolithium compounds to form complexes with dimethyl sulfide. The insoluble complex obtained here had the composition



In general form such compounds can be written as  , where Me is an alkali metal,

and R, R^1 and R^{11} are alkyl radicals. Although it is probable that complexes of greater complexity than those isolated by us can participate in the polymerization process, the influence of complex-forming additions on the chain structure can be depicted as being in accord with the representations of Ziegler [5] that the polymerization process is a consecutive organometallic synthesis. For the given case this scheme can be depicted as follows

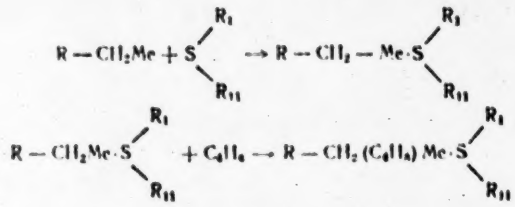


TABLE 1

Polymerization of Divinyl with Butyllithium at 50° in Petroleum Ether Solution in the Presence of Added Oxygen, Alcohol or Phenol

Exp. No.	Name of additive	Butyllithium concentration, mole % to the monomer	Concentration of additive, mole % to the monomer	% of 1,2 links in the polybutadiene
1	Without additive	0.040	—	12
2		0.055	—	11
3		0.056	—	10
4		0.060	—	10
1	Oxygen	0.050	0.018	32
2		0.050	0.037	21
3		0.057	0.037	43
4		0.057	0.037	33
5		0.060	0.011	28
6		0.130	0.011	29
1	Lithium benzylate*	1.36	5.30	39
2		1.36	5.30	37
1	Lithium phenolate*	0.15	5.79	35
2		0.15	5.79	33

TABLE 2

Polymerization of Divinyl with Butyllithium at 50° with Additions of Dialkyl Sulfides in Petroleum Ether Solution

Exp. No.	Name of additive	Butyllithium concentration, mole % to the monomer	Concentration of additive, mole % to the monomer	% of 1,2 links in the polybutadiene
1	Without additive	0.040	—	12
2		0.060	—	10
3		0.30	—	11
4		0.30	—	12
1	Dimethyl sulfide	0.14	61.74	62
2		0.19	82.0	68
1	Dipropyl sulfide	0.66	0.202	29
2		0.22	2.49	31
1	Diisopropyl sulfide	0.28	57.3	28
		0.28	57.3	25

* The benzylate and phenolate are shown, since the reaction of butyllithium with hydroxyl-containing additives leads to the formation of these substances even before the monomer is introduced into the system.

In view of the fact that the complex-forming additive is bound directly to the metal of the organometallic compound, it exerts an influence on the character of the carbon-metal bond during the whole process of forming the chain and in that way it exerts an influence on the structure of the polymer.

LITERATURE CITED

[1] A. Morton, Ind. and Eng. Chem., 42, 1488 (1950); J. Am. Chem. Soc. 69, 1675 (1947).

[2] K. Ziegler, E. Holzkamp, A. Breil and H. Martin, Angew. Chem., 67, 541 (1955).

[3] G. Natta, Makromol. Chem. 16, 213 (1955).

[4] B. A. Dolgopolsk, V. A. Kropachev and N. I. Nikolaev, Proc. Acad. Sci. USSR, 110, 789 (1953).*

[5] K. Ziegler, et al., Lieb. Ann. 473, 57 (1928).

Institute of High-Molecular Compounds
Academy of Sciences of the USSR

Received January 24, 1957

* Original Russian pagination. See C. B. Translation.

BLANK
PAGE

THE INFLUENCE OF SUBSTITUENTS ON THE STRENGTH OF FERROCENECARBOXYLIC ACIDS

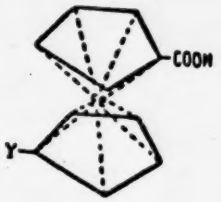
Nik. A. Nesmeyanov and O. A. Reutov

(Presented by Academician A. N. Nesmeyanov, March 1, 1957)

As is known, ferrocene shows the properties of an aromatic compound in substitution reactions [1-8]. In the present study we throw some light on the related problem of transmission of the mutual influence of substituents through the ferrocene nucleus.

We prepared the ferrocenecarboxylic acids of general formula I (Y = $-C_2H_5$, $-C_4H_9$, $-H$, $-COOCH_3$, $-COC_2H_5$, $-COCH_3$) and measured their dissociation constants.

Acetylferrocenecarboxylic acid was obtained by the Friedel-Crafts reaction from the methyl ester of ferrocenecarboxylic acid with subsequent saponification of the formed product. The position of the substituents in this compound was shown by its oxidation to the ferrocenedicarboxylic acid described by Woodward, the carboxyl groups of which are located in different rings, which had been established by various methods [4,9,10]. Ethylferrocenecarboxylic acid was obtained by the Clemmensen reduction of acetylferrocenecarboxylic acid, and consequently it has the same arrangement of the substituting groups. Butyrylferrocenecarboxylic acid was obtained by the Friedel-Crafts reaction, and its reduction gave butylferrocenecarboxylic acid.* The infrared spectrum of the methyl ester of the first of these acids (the 1000 and 1107 cm^{-1} frequencies, characteristic for an unsubstituted ring, are absent), and also its method of preparation (similar to that used for the preparation of diacetylferrocene and acetylferrocenecarboxylic acid), testify to the fact that the substituents are found in different rings. The monomethyl ester of ferrocenedicarboxylic acid was obtained by the incomplete hydrolysis of the dimethyl ester.



I

The dissocaition constants of the acids obtained by us, and also those of ferrocenecarboxylic, butyric and benzoic acids, are given in Table 1.

A comparison of the dissociation constants of the ferrocenecarboxylic acids reveals that the introduction of an alkyl group in the unsubstituted ring of the ferrocenecarboxylic acid lowers the dissociation constant, while the introduction of a negative substitutent raises it. Thus, acetylferrocenecarboxylic acid is 2.4 times stronger than ferrocenecarboxylic acid and 3.3 times stronger then ethylferrocenecarboxylic acid.

In the benzene series p-acetylbenzoic acid is 4.2 times stronger than benzoic acid [11], while p-carbomethoxybenzoic acid is 3.8 times stronger than the latter (in 50% ethanol by volume) [12]. As a result, the influence of substituents in the other ring of the molecule on the dissociation constant of ferrocenecarboxylic acid is fully comparable to the influence of these same substituents in the p-position on the dissociation constant of benzoic acid.

The fact that the influence of substituents in one of the ferrocene rings is transmitted to the other ring is

* The synthesis of the butyryl- and butylferrocenecarboxylic acids, and also the determination of their dissociation constants, was done jointly with G. N. Lapshin.

also supported by our work on the sulfonation of ferrocene in the presence of an equimolar amount of ferrocenecarboxylic acid (concurrent sulfonations). Here the ferrocenecarboxylic acid does not change, while the ferrocene shows almost complete sulfonation. We were able to sulfonate the ferrocenecarboxylic acid under more drastic conditions. As a result, the carboxyl group exerts a passivating influence on the unsubstituted ring of the molecule.

It should be mentioned that all of the systems that have been well studied up to now, effectively transmitting a mutual influence, have an unbroken chain of carbon atoms. In principle the ferrocene molecule is different in that in it one of the links of the transmitting system is the iron atom.

Preparation of Acetylferrocenecarboxylic Acid. To a mixture of 5.0 g (0.037 mole) of aluminum chloride, 2.35 g (0.030 mole) of acetyl chloride and 30 ml of CCl_4 with cooling to +10° was added in 15 minutes a solution of 5 g (0.0205 mole) of the methyl ester of ferrocenecarboxylic acid. After standing for 1 hour with periodic stirring the mixture was treated with ice water. The substance obtained after removal of the solvent was recrystallized from methanol; yield 3.2 g (58% of theory). After two recrystallizations from ligroin the methyl ester of acetylferrocenecarboxylic acid melts at 92.5-94.5°.

Found %: C 58.78; 58.69; H 5.05, 5.02; Fe 19.46, 19.43. $C_{14}H_{14}FeO_3$. Calculated %: C 58.77; H 4.94; Fe 19.52.

The methyl ester of acetylferrocenecarboxylic acid was saponified by heating with 20% NaOH. After two recrystallizations from benzene the m.p. of acetylferrocenecarboxylic acid is 153-155°.

TABLE 1

Acid	66% CH_3OH, 20°	
	$K_a \cdot 10^5$	pK_a
$CH_3CH_2CH_2COOH$	0.30	6.52
$C_5H_5-C_5H_4-Fe-C_5H_4-COOH$	0.31	6.50
$C_5H_5-C_5H_4-Fe-C_5H_4-COOH$	0.37	6.43
$H-C_5H_4-Fe-C_5H_4-COOH$	0.51	6.29
$CH_3OOC-C_5H_4-Fe-C_5H_4-COOH$	0.83	6.08
$C_2H_5OC-C_5H_4-Fe-C_5H_4-COOH$	1.13	5.95
$CH_3OC-C_5H_4-Fe-C_5H_4-COOH$	1.25	5.91
C_6H_5-COOH	1.17	5.93

Found %: C 57.74, 57.58; H 4.47, 4.33; Fe 20.34, 20.15. $C_{13}H_{12}FeO_3$. Calculated %: C 57.38; H 4.45; Fe 20.52.

Preparation of Ethylferrocenecarboxylic Acid. A suspension of 7 g of acetylferrocenecarboxylic acid in 50 ml of acetic acid was added to amalgamated zinc (prepared from 20 g of powderlike zinc and 1.5 g of mercuric chloride). To the mixture with stirring was added 20 ml of hydrochloric acid, and the same amount was again added after 90 minutes. The mixture was heated at 70° for an hour, and then it was diluted with a double volume of water; the obtained precipitate was filtered, and then repeatedly extracted with hot chloroform; the solvent was vacuum-distilled. Yield 4.9 g (70% of theory). After recrystallization from ligroin and ethanol, m.p. 75.5-77.5°.

Found %: C 60.58, 60.44; H 5.27, 5.48; Fe 21.89, 21.77. $C_{13}H_{14}FeO_2$. Calculated %: C 60.50; H 5.47; Fe 21.64.

Preparation of Butyrylferrocenecarboxylic Acid. The methyl ester of butyrylferrocenecarboxylic acid was obtained in 45% yield in the same manner as the methyl ester of diacetylferrocenecarboxylic acid; m.p. 54.5-55.5°.

Found %: C 61.86, 61.75; H 5.90, 5.89; Fe 17.63, 17.51. $C_{16}O_{18}FeO_3$. Calculated %: C 61.21; H 5.81; Fe 17.89.

Saponification of this ester gave butyrylferrocenecarboxylic acid. After recrystallization from CCl_4 and methanol, m.p. 114-115°.

Found %: C 60.36, 60.14; H 5.52, 5.38; Fe 17.71, 17.50. $C_{15}H_{16}FeO_3$. C 60.01; H 5.37; Fe 17.61.

Preparation of Acetylferrocenecarboxylic Acid. Butylferrocenecarboxylic acid was obtained by the same method as ethylferrocenecarboxylic acid. It was recrystallized from ligroin and methanol. Yield 74%; m.p. 73-74.5°.

Found %: C 63.16, 63.05; H 6.59, 6.45; Fe 19.41, 19.34. $C_{13}H_{14}FeO_3$. Calculated %: C 62.96; H 6.34; Fe 19.52.

Oxidation of Acetylferrocenecarboxylic Acid. A mixture of 0.7 g (0.0026 mole) of acetylferrocenecarboxylic acid and 0.9 g (0.0036 mole) of iodine was heated in 1 ml of pyridine at 100° for two hours, after which 10 ml of 15% NaOH was added, and the mixture was heated on the boiling water bath for another two hours. Then the reaction mass was diluted with 20 ml of hot water and filtered. Treatment of the filtrate with hydrochloric acid gave a mixed precipitate of ferrocenedicarboxylic and starting acid; the latter was extracted with hot benzene. The residue was recrystallized from acetic acid to give 0.1 g of ferrocenedicarboxylic acid, which was methylated with diazomethane. Recrystallization from methanol gave 0.06 g of the dimethyl ester of ferrocenedicarboxylic acid with m.p. 114-115°, which was not depressed when mixed with the authentic substance (from the literature, m.p. 114-115° [4]).

Preparation of Monomethyl Ester of Ferrocenedicarboxylic Acid. The monomethyl ester of ferrocenedicarboxylic acid was obtained by the 50-minute heating of 4.5 g (0.015 mole) of the dimethyl ester of ferrocenedicarboxylic acid with 0.6 g (0.015 mole) of NaOH, 2 ml of water and 60 ml of methanol; m.p. 147.5-149.5°. Yield 1.05 g (24.5% of theory).

Found %: C 54.75, 54.73; H 4.50, 4.43; Fe 19.42, 19.27. $C_{13}H_{12}FeO_3$. Calculated %: C 54.30; H 4.20 Fe 19.38.

Sulfonation of the Methyl Ester of Ferrocenecarboxylic Acid. A solution of 1.9 g (0.0078 mole) of the methyl ester of ferrocenecarboxylic acid in 20 ml of dry dichloroethane, cooled to +5°, was treated in portions with an earlier prepared solution of 1.2 g (0.015 mole) of sulfur trioxide and 3.0 g (0.034mole) of dioxane in 20 ml of dichloroethane. The mixture was allowed to stand in a closed vessel at 0° and in 24 hours was gradually added with stirring to an ice-cooled ether solution of diazomethane (three-fold excess of diazomethane). After standing for an hour the solution was filtered, washed with water, and the solvent vacuum-distilled. The dimethyl ester of ferrocenesulfocarboxylic acid was recrystallized from ligroin and methanol; m.p. 93-95°; yield 0.9 g (34% of theory).*

Found %: C 45.95, 46.08; H 4.09, 4.25. $C_{13}H_{14}FeO_5S$. Calculated %: C 46.16; H 4.17.

Concurrent Sulfonations. A mixture of 2.30 g (0.01 mole) of ferrocenecarboxylic acid and 1.86 g (0.01 mole) of ferrocene was dissolved in 250 ml of dichloroethane, the solution cooled to +5°, and to it was added in drops the earlier prepared solution of 0.85 g (0.0105mole) of sulfur trioxide and 4 g (0.045 mole) of dioxane in 15 ml of dichloroethane in 45 minutes. After standing for an hour at 5° and for 16 hours at 15-20° the solvent was vacuum-distilled and the residue was treated with 25 ml of 5% NaOH. The solution was filtered to give 0.18 g (10%) of ferrocene on the filter. Treatment of the filtrate with hydrochloric acid gave a precipitate of 2.0 g (90%) of ferrocenecarboxylic acid, and ether extraction of the filtrate gave another 0.10 g (4%) of this acid. The solvent was removed from the remaining solution in a current of air with moderate heating, and the sodium salt of ferrocenesulfonic acid was recrystallized from water to give 1.2 g of the substance. After recrystallization the benzylthiuronium salt of ferrocenesulfonic acid melts at 219-221° (from the literature, m.p. 220-222° [3]).

Determination of the Dissociation Constants. The dissociation constants were determined potentiometrically in aqueous methanol (68 wt. % methanol) at 20°. The following formulas were used to make the calculations

* Ferrocenecarboxylic acid can be sulfonated in the same manner.

$$K_a = [H^+]\frac{[NaOH]+[H^+]}{M-([NaOH]+[H^+])};\quad pK_a = pH + \log\frac{M-([NaOH]+[H^+])}{[NaOH]+[H^+]}.$$

where M is the molar concentration of the acid in solution, which was always taken equal to $5.0000\cdot10^{-3}$M. The pH values for each acid were measured for three different degrees of neutralization, so that the NaOH concentration in these buffer solutions was: 1) $1.4145\cdot10^{-3}$M, 2) $2.3575\cdot10^{-3}$M, 3) $3.3005\cdot10^{-3}$M.

An LP-4 potentiometer was used to make the pH measurements, and a buffer with pH 7.09 was used to calibrate the potentiometer scale. The difference between the individual pK_a values, calculated by the given formula, did not exceed 0.03 pK_a units for each acid.

LITERATURE CITED

[1] A. N. Nesmeyanov, Resumes des Communications XIV Congres International de Chimie pure et appliquee, Zürich, ref. No. 296, 1955.

[2] V. Weinmayr, J. Am. Chem. Soc. 77, 3009 (1955).

[3] A. N. Nesmeyanov, E. G. Perevalova and S. S. Churanov, Proc. Acad. Sci. USSR, 114, No. 2 (1957).*

[4] R. B. Woodward, M. Rosenblum and A. G. Whiting, J. Am. Chem. Soc., 74, 3458 (1952).

[5] A. N. Nesmeyanov and N. S. Kochetkova, Proc. Acad. Sci. USSR, 109, 543 (1956).*

[6] A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya and O. A. Nesmeyanova, Proc. Acad. Sci. USSR, 97, 459 (1954).

[7] R. Benkeser, D. Goggin and G. Schroll, J. Am. Chem. Soc., 76, 4025 (1954).

[8] R. Riemschneider and D. Helm, Ber. 89, 155 (1956).

[9] A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya, T. V. Nikitina and N. A. Simukova, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1956, 739.*

[10] H. H. Richmond and H. Freiser, J. Am. Chem. Soc., 77, 2022 (1955).

[11] F. G. Bordwell and G. D. Cooper, J. Am. Chem. Soc., 74, 1058 (1952).

[12] F. G. Bordwell and P. J. Boutan, J. Am. Chem. Soc., 78, 854 (1956).

[13] W. D. Kummler, J. Am. Chem. Soc., 60, 853 (1938).

Received February 26, 1957

* Original Russian pagination. See C. B. Translation.

SYNTHESIS AND DEHYDRATION OF UNSATURATED SILICON-CONTAINING ALCOHOLS

Correspondent Member A. D. Petrov, L. L. Shchukovskaya, S. I. Sadykh-Zade and Yu. P. Egorov

As is known, the dehydration character of alcohols is determined by their structure and the nature of the alcohol group (usually the tertiary alcohols are most easily dehydrated, followed by the secondary alcohols, with the primary alcohols being the most difficult to dehydrate). In the case of the silicon-containing alcohols the indicated factors are also supplemented by the influence of the silicon atom.

It was shown in a number of studies [1] that alcohols with the alcohol group in the β-position to the Si, both saturated and unsaturated, depending on their structure, usually undergo more or less β-decomposition together with dehydration. Unsaturated alcohols with the alcohol group in the γ-position, and also the β-alcohols that do not undergo decomposition, both being the subject of the present investigation, have been studied very little. The first unsaturated alcohols with the OH group in either the γ- or β-position were synthesized by the reactions [2,4].

$$CH_2=\underset{Cl}{\underset{|}{C}}-CH=CH_2OH + ClSiR_3 \xrightarrow{C_5H_5N} CH_2=\underset{Cl}{\underset{|}{C}}-CH=CH_2-O-SiR_3 \xrightarrow[Cl\,Si\,R_3]{Na} \rightarrow R_3Si-\underset{CH_3}{\underset{|}{C}}=CH-CH_2OSiR_3 \xrightarrow[HCl]{H_2O} R_3Si-\underset{CH_3}{\underset{|}{C}}=CH-CH_2OH$$

Their dehydration has not yet been studied.

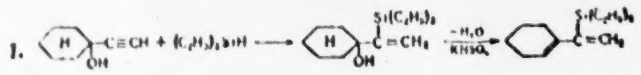
The first unsaturated alcohol with an OH group in the β-position and not undergoing decomposition was obtained [3] by the reaction

$$OH-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-C\equiv CH + (C_2H_5)_2SiH \rightarrow OH-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-\underset{Si(C_2H_5)_2}{\underset{|}{C}}=CH_2$$

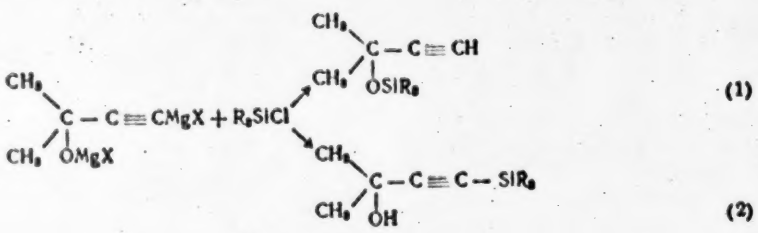
Its dehydration with $KHSO_4$ went with great ease and gave the first silicon analog of methylisoprene.

$$OH-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-\underset{Si(C_2H_5)_2}{\underset{|}{C}}=CH_2 \xrightarrow{-H_2O} CH_2=\underset{Si(C_2H_5)_2}{\underset{|}{C}}-C=CH_2$$

Continuing this investigation in the present study, we synthesized the cyclic analogs of the indicated alcohol and the silicohydrocarbon by the reactions:



As early as 1953 it was shown [4], after reacting dimethylacetylenylcarbinol with excess Grignard reagent, that the obtained derivative reacts with R_3SiCl. Of the two possible courses for this reaction to proceed:

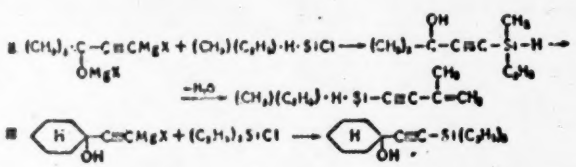


(1)

(2)

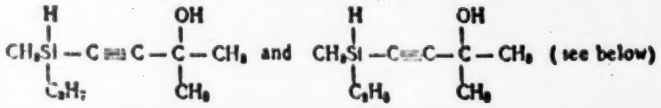
at the time, due to inability to dehydrate the obtained compound with iodine and on the basis of some spectral data, preference was given to the first variation shown above.

We repeated the synthesis of the above indicated compound for R = CH_3 and obtained a number of its analogs. All of these compounds were readily dehydrated with $KHSO_4$. The indicated results and a refinement of the spectral data permit the conclusion that this reaction proceeds in accord with equation (2).



To confirm the course of the reaction (in accord with equation (2)) by spectral methods proved possible due to our having recently obtained as standards the Raman spectra of a number of organosilicon compounds with a triple bond. The position of the characteristic C≡C frequency proved to be the following: $(CH_3)_2SiC{\equiv}C{-}CH_3$ 2186 cm^{-1}, $(CH_3)_2SiC{\equiv}C{-}C_4H_9$ 2175 cm^{-1}, $(CH_3)_2Si{-}C{\equiv}C{-}CH{=}CH_2$ 2154 cm^{-1}, $(CH_3)_2SiCH_2{-}CH_2C{\equiv}CH$ 2116 cm^{-1}. From the presented values it can be seen that when the C≡C bond is in the α-position to the Si and not at the end of the chain) a line in the 2170-2190 cm^{-1} region is observed, while with conjugation of the C≡C and C=C bonds the frequency drops to ~2155 cm^{-1}, and when the shift is to the end of the chain (and removal from the Si atom) the frequency drops to 2116 cm^{-1}. The last figure is quite close to the value observed for 1-alkynes (for example, R−C≡CH ~2120 cm^{-1}).

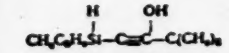
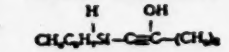
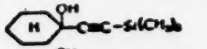
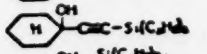
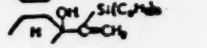
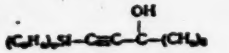
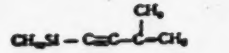
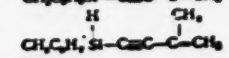
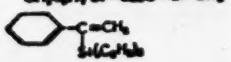
The Raman spectra obtained for alcohols



(see below)

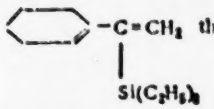
TABLE 1

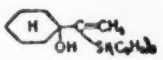
Properties of Unsaturated Organosilicon Alcohols and Corresponding Silicohydrocarbons

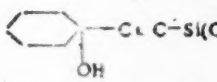
	B. p. °C/mm	M. p.°C	n_D^{20}	d_4^{20}	MR found	MR calcd.	Yield, %	Found, % C	Found, % H	Found, % Si	Calculated, % C	Calculated, % H	Calculated, % Si	Number of OH groups
Alcohols														
	82.5/10.5	—	1.4510	0.8606	48.85	49.00	65	61.63	10.44	16.12	61.54	10.30	17.55	—
	86/12	—	1.4515	0.8568	53.47	53.63	66	62.69	10.67	16.60	62.53	10.50	16.47	—
	127/24	71.5—72.5	—	—	—	—	—	—	—	—	—	—	—	1.06
	161.5—162/22	—	1.4522	0.9195	73.94	74.20	43	—	—	—	—	—	—	0.92
	169.5—170.5/22	—	1.4675	0.9163	75.56	75.53	95	—	—	—	—	—	—	0.97
	226/5	117.5—118.5	—	—	—	—	85							0.96
Hydrocarbons														
	120/754	—	1.4515	0.7867	47.37	46.72	80	69.60	10.27	20.40	69.6	10.15	20.29	
	141.5—143/745	—	1.4561	0.7948	47.40	46.96	95	67.77	9.74	22.67	67.66	9.72	22.60	
	86—87/9	—	1.4590	0.8067	51.96	51.61	75	71.14	10.54	18.20	71.05	10.53	18.42	
	161.5—163.5/24	—	1.5028	0.8811	76.50	73.81	70	75.64	12.15	—	75.60	11.79	—	

were found to contain an intense frequency at 2167 cm^{-1}. The position of this frequency is somewhat below the region indicated earlier for the $\gtrless Si-C\equiv C-R$ group, but is considerably higher than when at the end of the chain, as could have been expected if the reaction had gone in accord with equation (1). In addition, the infrared spectra of these alcohols showed the band typical of the OH group in the region of 2.75 μ.

Another confirmation of the structure was the formation of compounds of the enyne type. The spectra of two of the compounds in this series, $(CH_3)_3Si-C\equiv C-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2$ and $(C_2H_5)_3Si-C\equiv C-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle H}{\overset{|}{C}}}}=CH_2$, showed frequencies that corresponded to both the double and triple bonds, and specifically: ν (C=C) 1610 cm^{-1} and ν (C≡C) 2152 cm^{-1}. The obtained values are close to those indicated by us earlier for the vinylethynylsilanes $R_3SiC\equiv C-CH=CH_2$ [5].

It is interesting to mention that in the Raman spectrum of  the frequency of the C=C bond is raised to 1633 cm^{-1}, which is considerably higher than the value for $CH_3-\underset{\displaystyle Si(CH_3)_3}{\underset{|}{C}}=CH_2$ (1605 cm^{-1}).

1. Synthesis of  . In an autoclave was placed 15 g of acetylenylcyclohexanol, 15 g of triethylsilane and catalytic amounts of Pt/C. The autoclave was heated for 24 hours at 200-210°. The alcohol was isolated by fractional distillation, and had the constants given in Table 1.

2. Synthesis of  . To the ethylmagnesium bromide, prepared from 7.2 g of magnesium and 33.0 g of ethyl bromide in ether, was added an ether solution of 19.0 g of acetylenylcyclohexanol. The next day 27.0 g of triethylbromosilane was added, the reaction mass stirred for 3 hours with heating, the ether removed by distillation, and the residue heated in an oil bath at 100-130° for 3 hours. Then the reaction mixture was decomposed with water under ice cooling and extracted with ether. The ether extracts were dried over potash, the ether distilled off, and the residue was fractionated to give a product with the properties given in Table 1.

All of the other organosilicon alcohols were obtained in a similar manner.

The apparatus used to obtain the Raman spectra was an ISP-51 spectrograph with chamber f = 270 mm.

We were also able to synthesize the ether $\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-C\equiv CH$ under the conditions given below. Triethylchlorosilane (25 g) was gradually added with stirring to a mixture of 15 g of dimethylacetylenylcarbinol and 18 g of pyridine. To complete the reaction the flask was heated for 1.5 hours on the water bath. After cooling the precipitate was filtered, and the filtrate was distilled. The ether was isolated with b.p. 93.5° (183.7-184.2° and

758.8 mm) $n_D^{29} = 1.4310$, $d_4^{29} = 0.8414$.

Found %: H – 11.39; C – 66.83; Si – 13.92. $C_{11}H_{22}SiO$. Calculated %: H – 11.11; C – 66.66; Si – 14.14.

The isomeric tertiary alcohol, assumed by us earlier to be the ether [4], has b.p. 121.8° at 27 mm, $n_D^{20} = 1.4557$, $d_4^{29} = 0.8638$.

LITERATURE CITED

[1] F. C. Whitmore, L. H. Sommer, J. Gold, R. E. Van Strien, J. Am. Chem. Soc. 69, 1551 (1947); A. D. Petrov, V. A. Ponomarenko and A. D. Snegova, Proc. Acad. Sci. USSR, 112, No. 1, 79 (1957); S. I. Sadykh-Zade, D. Avgushevich and A. D. Petrov, Proc. Acad. Sci. USSR, 112, No. 3 (1957).*

[2] A. D. Petrov, V. F. Mironov and V. G. Glukhovtsev, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1958, 461.*

[3] L. L. Shchukovskaya and A. D. Petrov, J. Gen. Chem., No. 1, 3338 (1956).*

[4] A. D. Petrov, L. L. Shchukovskaya and Yu. P. Egorov, Proc. Acad. Sci. USSR, 93, No. 2, 293 (1953).

[5] A. D. Petrov, S. I. Sadykh-Zade and Yu. P. Egorov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, 722.*

The N. D. Zelinsky Institute
of Organic Chemistry
Academy of Sciences of the USSR

Received March 23, 1957

* Original Russian pagination. See C. B. Translation.

BLANK
PAGE

TAUTOMERISM OF ARYLAZOTROPOLONES

Acad. Sci. USSR Correspondent Member M. M. Shemyakin, F. A. Mendelevich,
A. M. Simonov and V. B. Petrinska

As is known, tropolones without substituents in the 5 position readily couple with diazonium salts. The usual products of this reaction are the arylazotropolones, which are assigned structure I [1].

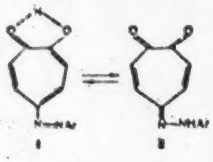
However, in studying the properties of some arylazotropolones, we encountered several years ago such properties of these compounds as were contradictory to formula I. This caused us to make a more profound study of the arylazotropolones, during which we came to the conclusion that these compounds are capable of tautomeric transformations into tropoquinone hydrazones (II). In its character the (I) ⇌ (II) tautomerism of the arylazotropolones discovered by us is comparable to the similar tautomeric transformations of the 5-nitro- and 5-nitroso-tropolones [1,2], and also of the aromatic hydroxyazo compounds. The first results of studying the tautomerism of the arylazotropolones is the subject of the present communication.

The studies discussed here were made with a group of 5-arylazotropolones (IV), obtained by the azo-coupling of the corresponding tropolones (III) with diazonium salts. The tendency of these compounds to react in the tautomeric form V was shown by us at the start in their ability to readily react with o-phenylenediamine to yield quinoxaline derivatives (VI), which, as is known, is not peculiar to the tropolones; the quinoxaline derivatives (VI) were obtained from arylazotropolones IVa-IVc. On the other hand, it was found that arylazotropolones IVd-IVf cleave with extreme ease (already when heated in CH_3OH) the carboxyl group found in the 3 position, migrating into the corresponding 5-arylazo-4-carboxymethyltropolones (VII); this reaction is not peculiar to the starting tropolone IIId [3], from which arylazotropolones IVd-IVf were obtained, but it is completely natural for the tautomeric forms Vd-Vf, where the cleaved carboxyl group is found in the β-position to one of the carbonyl groups. Finally, it was established that in the transformation of arylazotropolones IVd-IVf to acids (VII), and also directly from the latter, neutral compounds (VIII) are easily obtained, formed as the result of closure of the heterocycle in the tropoquinone hydrazone forms of the arylazotropolones.* The infrared spectra of the isolated compounds indicate that they contain the α-ketol grouping (see VIII), while their tendency to form quinoxaline derivatives with o-phenylenediamine is evidence of their ability to react in the tautomeric form (IX); that the amide grouping was present in the molecules was established when the infrared spectra of the obtained quinoxaline derivatives was studied.**

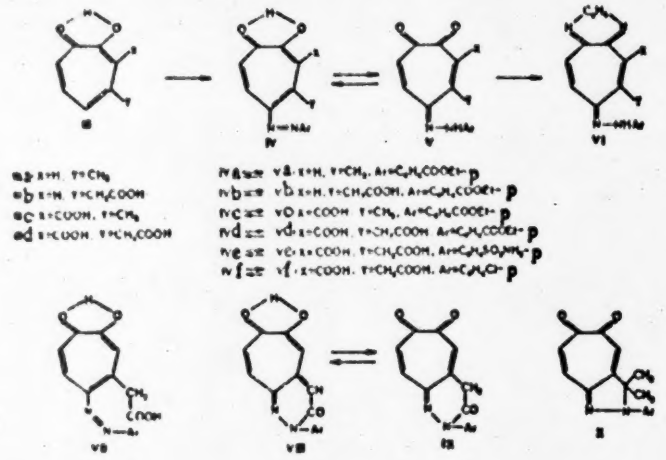
The data on the tropoquinone hydrazone tautomerism of the arylazotropolones I ⇌ II, obtained as the result of chemical study, was then confirmed by the spectroscopic investigations. It is known [6,7] that the tautomeric transformations of aromatic hydroxyazo compounds, leading to the appearance of their quinone hydrazone form in solution, is accompanied by the appearance of a second absorption maximum in the visible portion of the spectrum (for example, 4-phenylazo-1-naphthol in alcohol solution has two maxima—at 470 and 410 mμ [6]); here the maximum, lying in the longer wavelength region, usually belongs to the quinone hydrazone form.

* In their character these transformations are to a certain degree comparable with the process for the formation of quinopurpurins (X) [4], which, the same as compounds (VIII), can be regarded as being derivatives of the tropoquinone hydrazone forms of the arylazotropolones.

** Thus, the spectrum of compound VIII (Ar = C_6H_5Cl-p) showed the valence vibration band of the -O-H ..... group (a frequency of 3270 cm^{-1} in crystals and 3325 cm^{-1} in CCl_4), characteristic for α-ketols in which the hydroxyl group is included in the system with π-electron reaction (see [5]). As regards the band of the amide carbonyl, then it is impossible to show it clearly in the spectrum of compound VIII (Ar = C_6H_5Cl-p), but it was found (a frequency of 1676 cm^{-1} in crystals) in the spectrum of the quinoxaline derivative of this compound (data of D. N. Shigorin).



while the maximum with the smaller wavelength corresponds to the starting azoid form of the hydroxyazo compound. A similar picture was observed when we studied the absorption spectra of some alcohol solutions of the arylazotropolones, for example, IVa and IVb. As can be seen from the data, given in Table 1 (Nos. 4 and 5), these substances show two maxima in the visible portion of the spectrum. The maximum with the greater wavelength (495-500 mμ) lies close to the maxima of 4-phenylazo-1-naphthol, its N-methyl derivative and especially, the quinopurpurin (X; Ar = $C_6H_4SO_2NH_2$-p); see Nos. 1, 3 and 6 in Table 1. Consequently, this long-wave maximum indicates the presence of the tautomeric tropoquinone hydrazone form (V) in the solutions of the investigated arylazotropolones. On the other hand, the maximum with the smaller wavelength (402 mμ), lying close to the corresponding maximum of 4-phenylazo-1-naphthol and to the maximum of its O-methyl derivative (see Nos. 1 and 2 in Table 1), corresponds to the azotropolone form IV of the arylazotropolones.



The ability of the arylazotropolones to undergo the above discussed tautomerism was recently mentioned by Nozoe [9], who, the same as we, found that these compounds form quinoxaline derivatives of the VI type with o-phenylenediamine. We wish to thank Prof. Nozoe for sending us some samples of the quinopurpurins, which greatly facilitated our spectroscopic investigations.

EXPERIMENTAL

1. Preparation of 5-Arylazotropolones IV)

A solution of the diazotized amine was added at 5° to an alkaline solution of the tropolone IIIa-IIIc [3, 10], the mixture was stirred for about an hour, and then acidified. The obtained precipitate was filtered, washed with water, recrystallized, and dried in vacuo at 40°.

Compound IVa. Orange crystals from glacial CH_3COOH. M.p. 187-188° (with decompn.). Yield 75%. Found %: C 65.20, H 4.93; N 9.20. $C_{17}H_{16}O_4N_2$. Calculated %: C 65.37; H 5.16; N 8.97. Compound IVb. Brown-red crystals from 80% CH_3COOH. M.p. 168-169° (with decompn.). Yield 61%. Found %: C 60.64; H 4.44; N 7.67. $C_{18}H_{16}O_6N_2$. Calculated %: C 60.67; H 4.52; N 7.86. Compound IVc. Dark-red crystals from glacial CH_3COOH. M.p. 179-180° (with decompn.). Yield 51%. Found %: C 60.69; H 4.52; N 7.78. $C_{18}H_{16}O_6N_2$. Calculated %: C 60.67; H 4.52; N 7.86. Compound IVd. Recrystallized from 80% CH_3COOH (1:30), heated for 1-2 minutes at 30°, and filtered rapidly. Brown-red crystals with m.p. 158-159° (with decompn.). Yield 40%.

Found %: C 56.79; H 3.84; N 6.63. $C_{19}H_{16}O_4N_2$. Calculated %: C 57.00; H 4.03; N 7.00.* Compound IVe Recrystallized at 30-40° in the same manner as compound IVd. Brown-red crystallohydrate with m.p. 174-175° (with decompn.); the water is removed at 105-110° and 3 mm. Yield 25%. Found %: C 45.20; H 3.65; N 9.95. $C_{16}H_{16}O_5N_2S \cdot H_2O$. Calculated %: C 45.17; H 3.55; N 9.88. Compound IVf. Recrystallized at 70° from glacial CH_3COOH (1: 13) in the same manner as compound IVd. Brown-red crystallohydrate with m.p. 145-146° (with decompn.). Yield 35%. Found %: C 50.33; H 3.35; N 7.65; Cl 9.60. $C_{16}H_{11}O_5N_2Cl \cdot H_2O$. Calculated %: C 50.47; H 3.44; N 7.36; Cl 9.31.

2. Preparation of Quinoxaline Derivatives (VI)

A dioxane solution of the azo compound IVa-IVc and an equivalent amount of o-phenylenediamine was boiled for 10-12 minutes. The precipitate was filtered, washed with dioxane, recrystallized, and dried at 70-80° and 1-3 mm.

Quinoxaline Derivative From IVa. Dark-red crystals from glacial CH_3COOH with m.p. 243-244° (with decompn.). Yield 63%. Found %: C 69.41; H 5.33; N 13.69. $C_{23}H_{20}O_2N_4 \cdot 0.5CH_3COOH$. Calculated %: C 69.55; H 5.35; N 13.52. Quinoxaline Derivative From IVb. Dark-red needles from glacial CH_3COOH with m.p. 221-222° (with decompn.). Yield 25%.** Found %: C 64.06; H 5.12; N 11.40. $C_{24}H_{20}O_4N_4 \cdot CH_3COOH$. Calculated %: C 63.92; H 4.95; N 11.47. Quinoxaline Derivative From IVc. Yellow-orange crystals from dioxane with m.p. 241-242° (with decompn.). Yield 79%.** Found %: C 67.30; H 4.83; N 13.00. $C_{24}H_{18}O_4N_4$. Calculated %: C 67.28; H 4.70; N 13.08.

3. Preparation of 5-Arylazotropolones (VII) and Compounds (VIII)

Decarboxylation of Azo Compound IVd. Two grams of IVd in 25 ml of methanol was heated for 3 hours at 60°. The amount of cleaved CO_2 and 91%. Without cooling, the precipitate was filtered, washed with warm methanol, and recrystallized from 80% CH_3COOH. Weight 0.37 g; m.p. 168-169° (with decompn.). The substance is identical with azo compound IVb; see Expt. 1. Concentration of the methanolic filtrate gave compound VIII (Ar = C_6H_4COOEt-p) as a precipitate, which was washed with soda solution and recrystallized from glacial CH_3COOH. We obtained 0.12 g of long yellow needles with m.p. 231° (with decompn.). The compound is insoluble in aqueous alkalies, but is colored a dark-red. Prior to analysis the substance was dried at 50° and 3 mm. Found %: C 63.44; H 4.19; N 7.86. $C_{18}H_{14}O_5N_2$. Calculated %: C 63.90; H 4.17; N 8.28.

Decarboxylation of Azo Compound IVe. Two grams of IVe in 40 ml of 65% methanol was heated for 50 minutes at 60°. Here 90% of the CO_2 was cleaved. Without cooling, the precipitate was filtered and washed with warm 65% methanol. We obtained 0.44 g of azo compound VII (Ar = $C_6H_4SO_2NH_2$-p), which crystallized from 80% CH_3COOH as dark-red plates with m.p. 200-201° (with decompn.). Cooling of the reaction filtrate resulted in the deposition of a second isomorphous form of the same azo compound (0.44 g), which crystallized from 80% CH_3COOH as slender yellow needles with m.p. 184-185° (with decompn.). The two isomorphic forms are easily transformed into each other during crystallization. Yellow form: Found %: C 50.00; H 4.03; N 11.30. Red form: found %: C 49.78; H 3.76; N 11.52. $C_{15}H_{13}O_6N_3S$. Calculated %: C 49.58; H 3.60; N 11.56.

Decarboxylation of Azo Compound IVf. Three grams of IV in 30 ml of methanol was heated for 2.5 hours at 60°. After cooling the precipitate was filtered, washed with methanol, and recrystallized from glacial CH_3COOH. We obtained 0.17 g of compound VIII (Ar = C_6H_4Cl-p) as long yellow needles with m.p. 258° (with decompn.). Prior to analysis the substance was dried at 45° and 25 mm. Found %: C 56.60; H 3.62; N 8.02. $C_{18}H_9O_5N_2Cl \cdot CH_3COOH$. Calculated %: C 56.59; H 3.63; N 7.77. The crystallization acetic acid is removed at 80-85° and 3 mm.

The substance is insoluble in aqueous alkalies, but is colored a dark-red. The heating of compound VIII (Ar = C_6H_4Cl-p) in dioxane solution with o-phenylenediamine yields the quinoxaline derivative with m.p. 269-270° (with decompn.) (from dioxane). Found %: C 67.57; H 3.82; N 15.02. $C_{28}H_{13}ON_4Cl$. Calculated %: C 67.65; H 3.52; N 15.03.

---

* The alkaline hydrolysis (boiling with 20% NaOH) of compound IVd leads to the formation of a number of substances of aromatic character, from which p-aminobenzoic acid was identified as the picryl derivative; about 20% of NH_3 is cleaved with acid hydrolysis (boiling with 5% H_2SO_4).

** The substance dissolves in aqueous alkalies only when heated (apparently it contains a lactone ring).

The reaction solution, remaining after the removal of compound VIII (Ar = C_6H_4Cl-p), was concentrated, the obtained precipitate was filtered, washed with methanol, treated with soda solution, again filtered, and the filtrate made acid. The resulting precipitate was filtered, washed with water, and recrystallized from glacial CH_3COOH. We obtained 0.12 g of azo compound VII (Ar = C_6H_4Cl-p) with m.p. 173° (with decompn.). Prior to analysis the substance was dried at 45° and 5 mm. Found %: C 56.34; H 3.65; N 8.84. $C_{15}H_{11}O_4N_2Cl$. Calculated %: C 56.52; H 3.48; N 8.78. When subjected to prolonged boiling in methanol solution the obtained azo compound gradually changed into compound VIII (Ar = C_6H_4Cl-p), which was isolated as described above.

TABLE 1

Expt. Nos.	Substance	Solvent*	λ_{max} in mμ	
1	4-phenylazo-1-naphthol	C_2H_5OH	410	470
2	4-phenylazo-1-naphthol O-methyl ether	C_2H_5OH	392	
3	1,4-naphthoquinone methylphenylhydrazone	C_6H_6		466
4	5-(p-carbethoxyphenyl)-azo-4-methyltropolone	C_2H_5OH	402	500
5	5-(p-carbethoxyphenyl)-azo-4-carboxymethyltropolone	C_2H_5OH	402	495
6	p-sulfanilamidoquinepurpurin	C_2H_5OH		502

* In the preparation of the arylazotropolone solutions it was necessary to heat them for several minutes at 60-70° to dissolve the substance. For the absorption spectra of the other arylazotropolones, described earlier in the literature, see [8].

LITERATURE CITED

[1] P. Pavson, Chem. Rev., 55, 9 (1955).

[2] T. Nozoe, et al., Science Rep. Tohoku Univ., 35, 275 (1952); 37, 408 (1953); Proc. Japan Acad., 29, 565 (1953).

[3] T. Nozoe, et al., Proc. Japan Acad., 29, 17 (1953); W. D. Crow, et al., J. Chem. Soc., 1952, 3705.

[4] T. Nozoe, et al., Proc. Japan Acad., 31, 455 (1955).

[5] D. N. Shigorin, et al., Proc. Acad. Sci. USSR, 108, 672 (1956).*

[6] R. Kuhn and F. Bär, Lieb. Ann., 516, 143 (1935); L. N. Ospenson, Acta Chem. Scand., 5, 491 (1951).

[7] A. Burawoy, et al., J. Chem. Soc., 1952, 4793; J. B. Müller, et al., Helv. Chim. Acta, 35, 2579 (1952); I. M. Klotz, et al., J. Am. Chem. Soc., 76, 5136 (1954).

[8] K. Yamane, Bull. Chem. Soc. Japan, 27, 168 (1954).

[9] T. Nozoe, et al., Proc. Japan, Acad, 32, 344 (1956).

[10] R. D. Haworth, et al., J. Chem. Soc., 1948, 1045, 1951, 561.

Institute of Biological and Medicinal Chemistry
Academy of Medical Sciences of the USSR,
Moscow Textile Institute

Received June 17, 1957

* Original Russian pagination. See C. B. Translation.

KINETICS OF CATALYTIC DEHYDROGENATION OF ISOPROPYL ALCOHOL IN PRESENCE OF TRANSITION METALS OF THE FOURTH PERIOD

Academician A. A. Balandin and P. Teteni

Few studies have been made of the kinetics of dehydrogenation of alcohols over iron, cobalt and nickel catalysts. A few papers have been published on the use of a nickel catalyst deposited on a support in a flow system [1,2] and without a support in a static system [3]. This reaction can also serve as a model in the study of the above-mentioned catalysts which are very extensively used in industry.

In the present work we investigated the kinetics of dehydrogenation of isopropyl alcohol over metallic iron, cobalt and nickel prepared by precipitation. The iron catalyst was obtained by precipitation of iron oxalate* with 50% iron sulfate solution. The precipitate was washed with distilled water until the wash waters gave a negative reaction for the sulfate ion, and it was then decomposed in a current of electrolytic hydrogen at 400° for 6 hours. Cobalt and nickel catalysts were prepared by precipitation of the corresponding hydrous oxides with ammonia from a 20% solution of the corresponding nitrate. The precipitate was washed with distilled water until the wash waters gave a negative reaction for the NO'_3 ion. The hydrous oxides of cobalt and nickel were decomposed in an air stream at 400°, and the resultant oxides were reduced with electrolytic hydrogen at 200, 250, 300 and 350° for 3 hours at each temperature. Between experiments the catalyst was regenerated with hydrogen for 45-60 minutes. The isopropyl alcohol and acetone used in the investigation had physical constants identical with those reported in the literature. Experiments were carried out in the usual flow apparatus [4]. It was found that in the investigated ranges (up to 250° for iron and cobalt, up to 215° for nickel) the catalysts lead exclusively to dehydrogenation of isopropyl alcohol to acetone. The gas evolved was found to be pure hydrogen by gas analysis. Distillation of the catalyst established that it consisted solely of acetone and unreacted alcohol.

As was shown earlier [2,5], the dehydrogenation of alcohols follows the general kinetic equation, derived by one of the authors [6], of monomolecular catalytic reactions in a stream. In the case of dehydrogenation of alcohols free of impurities, this equation has the form:

$$\frac{dm}{dl} = k \frac{(A_1 - m)}{A_1 + (z_2 + z_3 - 1)\, m}, \qquad (1)$$

where k is the velocity constant of the reaction, A_1 is the feed rate of the starting substance, z_2 and z_3 are the relative adsorption coefficients of the ketone and hydrogen, m is the amount of hydrogen evolved per minute, and l is the length of the catalyst bed.

Integration of equation (1) gives

$$k = (z_2 + z_3)\, A_1 \ln \frac{A_1}{A_1 - m} - (z_2 + z_3 - 1)m. \qquad (2)$$

* But not by reduction with hydrogen of oxides, which process is only completed at the temperature of appreciable sintering.

The relative adsorption coefficients entering into equation (2) were determined by a reaction-kinetic method based on the lowering of the reaction velocity on addition of a known quantity of reaction product to the starting substance. Comparison of the reaction velocity of the mixture with that of the pure substance shows the extent to which the added substance is adsorbed on the active particles of catalyst. The magnitude of the adsorption coefficients was calculated from the formula:*

$$z = \frac{B_1(2H - Y) - HY}{(1 - B_1)Y}, \qquad (3)$$

where $B_1 = A_1/\Sigma A_i$; $Y = m/\Sigma A_i$; $H = Y_0/(2 - Y_0)$. Here Y is the degree of transformation in experiments with mixtures of Y_1 is that with the pure substance.

The relative adsorption coefficients were determined from the velocity of dehydrogenation of binary mixtures of the reaction products with the starting alcohol. Here the space velocity of the alcohol in the experiment with the pure substance equalled the overall space velocity of the alcohol and the reaction product in experiments with mixtures. The constancy of the activity of the catalyst was checked by alternation of experiments with mixtures and experiments with the pure substance. Results of the determinations of adsorption coefficients are presented in Tables 1 and 2. The curves of adsorptive displacement, plotted from five points at each temperature, had the general form observed in [6,8].

TABLE 1

Relative Adsorption Coefficients z_2

Catalyst	Temperature °C	$Z_2 = a_{acet}/a_{alc.}$
Iron	210	0.66±0.02
	230	0.70±0.07
	240	0.71±0.06
Cobalt	206	0.45±0.03
	221	0.48±0.03
	238	0.45±0.03
Nickel	166	1.51±0.03
	182	1.35±0.06
	198	1.16±0.10
	209	1.00±0.02

TABLE 2

Relative Adsorption Coefficients z_3

Catalyst	Temperature °C	$z_3 = a_{H_2}/a_{alc.}$
Iron	200	0.20±0.02
	220	0.05±0.02
	235	0.06±0.02
	247	0.10±0.02
Cobalt	204	1.03±0.03
	223	1.02±0.06
Nickel	239	1.04±0.01
	172	0.39±0.01
	184	0.25±0.02
	197	0.16±0.01
	208	0.11±0.01

Tables 1 and 2 indicate that the relative adsorption coefficients of acetone and hydrogen on iron and cobalt catalysts not depend upon the temperature. Temperature-dependence of adsorption coefficients is observed only in the case of nickel on which the relative adsorption coefficients of both substances decrease with rising temperature. The temperature-dependence of these adsorption coefficients is logarithmic in form as shown in Fig. 1 where log z is plotted against 1/T. A logarithmic dependence of the relative adsorption coefficients on the temperature has also been observed in other studies [2,8] and is consistent with the concept of adsorption coefficients as equilibrium constants of the adsorption process. The differences between the heats of adsorption of hydrogen, acetone and isopropyl alcohol were calculated from the data with the help of the formula:

$$\lambda_{prod.} - \lambda_{alc.} = \frac{4.57\,(\log z'' / z')}{1/T_1 - 1/T_2} \qquad (4)$$

The following values were obtained: $\lambda_{acetone} - \lambda_{alcohol} = 3.7$ kcal/mol and $\lambda_{H_2} - \lambda_{alcohol} = 14.5$ kcal/mol.

* Calculation of the relative adsorption coefficients by an accurate method [7] shows that in the cases that we investigated the approximate formula (3) is sufficiently accurate for calculation of these values.

In the case of iron and cobalt the heats of adsorption of alcohol and reaction products are the same or very similar, as follows from the absence of a temperature dependence of the adsorption coefficients [9,10].

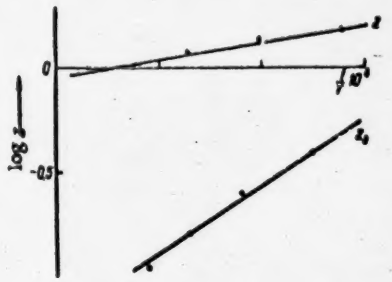


Fig. 1. Logarithm of the relative adsorption coefficients as functions of the reciprocal of the temperature on nickel catalyst.

The adsorption coefficients were also used for calculation of the velocity constants of the reaction at different temperatures. For the purpose of determination of the true energy of activation of dehydrogenation with each catalyst, a series of experiments was run at different temperatures and with constant space velocity. The values of A_1, $\underline{m}$ and $z_2 + z_3$ were substituted in formula (2) in order to calculate the velocity constants. For the nickel catalyst the value of $z_2 + z_3$ at the required temperature was found by interpolation of the plots of logarithmic dependence (Fig. 1). The results are set forth in Tables 3-5 and in Fig. 2. The linear dependence of log k on 1/T is in accord with the Arrhenius equation, which confirms the validity of equation (2). The true activation energy of dehydrogenation of alcohols over Fe and Co was determined for the first time. A value of ϵ = 9.9 kcal/mol was obtained in [2] for the dehydrogenation of 2-butanol over nickel on quartz, i.e., only slightly higher than in the present work.

TABLE 3

Dehydrogenation of Isopropyl Alcohol Over Iron; Volume of Catalyst 5.6 ml; Pass Velocity 0.15 ml/min; A_1 = 46 ml/min; A_1^1 = 8.03 ml/min on 1 ml Catalyst; $z_2 + z_3$ = 0.79; ϵ = 20,000 cal/mol; $k_0 = 7.08 \cdot 10^8$; $\epsilon/\log k_0 = 2.26 \cdot 10^9$

Exp. No.	Temp. °C	v_{H_2}, ml/min	$\frac{m_{H_2}}{V_1}$, ml/ml catalyst	h	$h_{calcd.}$
3	200	2.28	0.407	0.409	0.403
7	200	2.24	0.400	0.406	0.403
5	210	3.31	0.592	0.606	0.630
2	220	5.32	0.950	1.004	0.966
1	227	6.66	1.19	1.27	1.26
4	232	7.64	1.36	1.47	1.55
6	235	9.03	1.61	1.76	1.78

TABLE 4

Dehydrogenation of Isopropyl Alcohol Over Cobalt; Volume of Catalyst 7 ml; Pass Velocity 0.15 ml/min; A_1 = 45 ml/min; A_1^1 = 6.43 ml/min per 1 ml Catalyst; $z_2 + z_3$ = 1.49; ϵ = 12,400 cal/mol; $k_0 = 8.03 \cdot 10^8$; $\epsilon/\log k_0 = 2.1 \cdot 10^9$

Exp. No.	Temp. °C	v_{H_2}, ml/min	$\frac{m_{H_2}}{V_1}$, ml/ml catalyst	h	$h_{calcd.}$
5	183	5.80	0.828	0.943	0.890
7	189	6.25	0.894	1.00	1.05
8	194	7.33	1.05	1.20	1.21
6	198	8.67	1.24	1.44	1.38
2	199	8.90	1.27	1.49	1.42
3	210	11.20	1.60	1.98	1.88
1	211	10.98	1.57	1.92	1.95
4	218	13.20	1.89	2.33	2.42

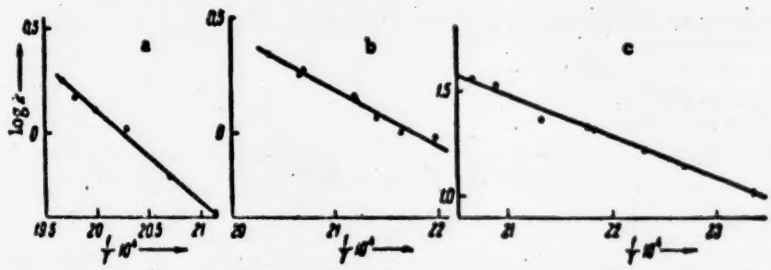


Fig. 2. Dependence of the logarithm of the velocity constant of dehydrogenation on the reciprocal of the temperature: a) on iron; b) on cobalt; c) on nickel.

TABLE 5

Dehydrogenation of Isopropyl Alcohol Over Nickel; Catalyst Volume 0.5 ml; Pass Velocity 0.15 ml/min; A_1 = 45 ml/min; A_1' = 90 ml/min per 1 ml Catalyst; c = 8,900 cal/mol, k_0 = $= 3.67 \cdot 10^8$; $c/\log k_0 = 1.9 \cdot 10^3$

Exp. No.	Temp. °C	V_{H_2} ml/min	ml H_2 per 1 ml catalyst	$z_2 + z_3$	k	$k_{calcd.}$
1	185	8.8	17.6	1.54	29.54	29.65
2	196	12.0	24.0	1.32	29.29	28.10
3	175	7.0	14.0	1.78	16.33	16.60
4	186	9.0	18.0	1.46	21.13	21.13
5	211	14.6	29.2	1.09	35.67	34.70
6	168	6.0	12.0	2.08	13.82	14.10
7	156	4.9	9.8	2.71	10.35	10.40
8	206	13.8	27.6	1.14	33.63	31.30

We see that the activation energy of dehydrogenation falls off from iron to nickel. The activity of catalysts of the transition metals of the fourth period rises with increasing atomic number of the metal and with decreasing interatomic distance.

The new results obtained in the present work are significant for calculation of the dependence of the catalytic activity of elements on their position in the Periodic System of Mendeleev.

LITERATURE CITED

[1] A. A. Balandin and A. M. Rubinshtein, J. Phys. Chem., 6, 576 (1935).

[2] A. A. Balandin and E. I. Klabunovsky, Proc. Acad. Sci. USSR, 98, 783 (1954).

[3] C. Thonon and J. C. Jungers, Bull. Soc. Chim. Belg., 58, 331 (1949); 59, 604 (1950).

[4] A. A. Balandin and P. Teteni, Proc. Acad. Sci. USSR, 113, No. 5, 1090 (1957).*

[5] A. E. Agronomov, Herald Moscow State Univ., 6, No. 2, 109 (1951).

[6] A. A. Balandin, J. Gen. Chem., 12, 153 (1942).

[7] A. A. Balandin, J. Gen. Chem., 12, 160 (1942).

[8] A. A. Tolstopyatova, A. A. Balandin and E. M. Dmitriev, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1956, 1404.*

[9] A. A. Balandin, Proc. Acad. Sci. USSR, 63, 33 (1948).

[10] A. Kh. Bork, Collected Studies on Phys. Chem. Acad. Sci. USSR Press, 1947, p. 168.

Moscow State University

Received March 23, 1957

* Original Russian pagination. See C. B. Translation.

CATALYSTS ON THE BASIS OF ALKYL MAGNESIUM HALIDES AND TITANIUM TETRACHLORIDE FOR THE SYNTHESIS OF AMORPHOUS AND CRYSTALLINE POLYMERS FROM α-OLEFINS AND DIENES

B. A. Dolgoplosk, L. M. Romanov, B. L. Erusalimsky and V. Ya. Bogomolnyi

(Presented by Academician I. N. Nazarov, April 25, 1957)

The preparation of polymers from aliphatic compounds of the ethylene series on the basis of initiation of polymerization by free radicals is only possible with the first member of the series (ethylene). Reaction of free radicals with homologs of ethylene leads to formation of low-molecular products due to chain-breaking reactions in the early stages of the process [1]. Ziegler and co-workers utilized the reaction between organoaluminum compounds and titanium tetrachloride for initiation of the polymerization of ethylene [2]. Further investigations in this field revealed [3] the possibility of polymerization of olefins with formation of polymers with homogeneous (isotactic) structure. It was later shown that organoaluminum compounds in Ziegler catalyst can be replaced by other organometallic derivatives, in particular by compounds of sodium and lithium. For example, the systems $C_6H_5Na - TiCl_4$ and $C_4H_9Li - TiCl_4$ also promote the polymerization of ethylene [4,5]. The mechanism of these reactions cannot yet be considered clarified. The reaction between the components of Ziegler catalyst is known to bear an oxidation-reduction character and leads to formation of titanium derivatives with a lower valence [6]. Formation of hydrocarbons such as ethane and ethylene has also been observed when using triethylaluminum. Very similar phenomena are also observed in the reaction between salts of heavy metals and organomagnesium compounds.

N. V. Kondyrev and D. A. Fomina [7] (who published the first work in this field) showed that reaction between alkyl magnesium halides and salts of various metals (iron, copper, cobalt, nickel, chromium and molybdenum) leads to formation of: a) equivalent quantities of saturated and unsaturated hydrocarbons corresponding to the alkyl of the organomagnesium compound; b) reduced forms of the heavy metals. Later study of these reactions [8-16] led to the conclusion that they proceed through the stage of formation of unstable organic compounds of the heavy metals, the decomposition of which is usually regarded as a free-radical process. On this basis it seemed probable that the reaction between organomagnesium halides and titanium tetrachloride enables us to obtain results analogous with those obtained by Ziegler and Natta with organoaluminum compounds. It must be pointed out that in reactions of the type under consideration, an important part is played by complex-forming agents (ethers, sulfides, oxygen) which can exert a considerable influence on the course of the process and on the chain structure. As we know, organomagnesium compounds form stable complexes with ether which are only decomposed by prolonged thermal treatment at 150°. We established that reaction of organomagnesium compounds of the R-MgHal type with $TiCl_4$ leads to formation of catalytic complexes which effectively initiate the polymerization of monomers only if the magnesium derivatives have previously been completely freed of ether. This was proved in the cases of ethylmagnesium chloride, ethylmagnesium bromide and octylmagnesium bromide. For experimental purposes it is convenient to use the organomagnesium compounds in the form of a dispersion in gasoline. Such dispersions are obtained by conducting the decomposition of the ether complex in a gasoline medium; in this manner a fine dispersion is formed which is extremely stable to moisture and retains its activity for a long period when kept in the air.

We demonstrated the effectiveness of the system R-MgHal-$TiCl_4$ for initiation of a polymerization process

in the cases of ethylene, propylene, styrene and isoprene. Polymerization of ethylene is realized without application of pressure or external heating. The reaction commences almost immediately after commencement of passage of ethylene through a suspension of the organomagnesium compound in gasoline containing a small quantity of titanium tetrachloride. The resultant polyethylene has $[\eta] = 2.55$ (measured in decalin at 135°), m.p. 130-138°, tensile strength 335 kg/cm^2 and relative elongation of 730%. These data are similar to those found for polyethylene prepared with the help of the usual Ziegler catalyst. The data that we obtained for the polymerization of propylene are of great interest. In one of the papers of Natta [11] it is pointed out that replacement of organoaluminum compounds in Ziegler catalyst by organomagnesium compounds excludes the possibility of obtaining isotactic polymers from α-olefins.

We showed that polymerization of propylene in presence of ethylmagnesium chloride and titanium tetrachloride gives approximately equal parts of amorphous and crystalline (isotactic) forms of polymer. The amorphous form (soluble in ether) has a vitrification temperature of −35° and $[\eta] = 0.57$ (in benzene). In addition a fraction insoluble in boiling hexane was isolated; its crystallinity was confirmed by spectroscopic and x-ray analysis.

Different polymer forms were likewise isolated in the polymerization of isoprene. Using the same components, the polymerization of isoprene gave: 1) a fraction soluble in benzene, containing 87% of cis-1,4 chains, and 2) an insoluble form containing (on the basis of infra-red examination) only trans-1,4 chains.*

The co-formation of cis-1,4-polyisoprene and trans-1,4-polyisoprene and of amorphous and isotactic polypropylene is direct evidence that the system contains catalytic complexes of various types, leading to formation of a polymer structure specific for a given complex.

EXPERIMENTAL

Synthesis of alkylmagnesium halides. Ether-free organomagnesium compounds were prepared by the Grignard procedure [12]; the solvent was distilled off from the ethereal solution of the organomagnesium derivative and the residue was heated for 30 hours at 150-160° in vacuum (10 mm). The resultant white, porous mass was pulverized in a nitrogen stream. A dispersion in gasoline was obtained by introducing the gasoline into the reaction flask after distillation of the main bulk of solvent.

Polymerization of ethylene. Thoroughly dried ethylene was passed into a suspension of ethylmagnesium chloride and $TiCl_4$ in a gasoline fraction (b.p. 90-110°) with intensive stirring. The initial temperature was 20°. At the end of the reaction the temperature had risen to 50°. Interruption of the polymerization process at a definite stage was effected by addition of alcohol.

Polymerization of propylene. The reaction was conducted in a 1.5-liter autoclave fitted with a stirrer; 500 ml gasoline was charged in together with the required amount of ethylmagnesium chloride and $TiCl_4$. Pressure 6-9 atm. Duration of reaction 1 hour at 80°. Yield of polymer 115 g.

Polymerization of isoprene. Into a 4-liter stirred autoclave were charged 1 liter gasoline, ethylmagnesium chloride, $TiCl_4$ and 0.5 liter isoprene. Duration of reaction 1 hour at 70-80°. Yield of polymer 200 g. The benzene-soluble fraction (63% of the total amount) contained 87% of cis-1,4- chains, 5% of trans-1,4 chains, 3% of 1,2-chains and 5% of 3,4-chains. The insoluble polymer was 100% 1,4-trans-polyisoprene.

Polymerization of styrene. 20 g of styrene was intensively stirred with a solution of 0.4 g $TiCl_4$ in 60 ml gasoline containing 0.5 g ethylmagnesium chloride in suspension, at 60° for 1 hour. Yield of polymer quantitative.

LITERATURE CITED

[1] E. B. Milovskaya, B. A. Dolgoplosk and B. L. Erusalimsky, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1957, 494.**

[2] K. Ziegler, E. Holzkamp, H. Breil and H. Martin, Zs. angew. Chem., 67, 541 (1955).

[3] G. Natta, J. Polymer. Sci. 16, 213 (1955).

* The spectroscopic and x-ray measurements were carried out by E. I. Pokrovsky and L. A. Volkova.

** Original Russian pagination. See C.B. Translation.

[4] C. Nenitzescu, Zs. angew. Chem., 68, 438 (1956).

[5] R. S. Aries, Rub. Age, 79, 812 (1956).

[6] G. Natta, Zs. angew. Chem., 68, 393 (1956).

[7] N. V. Kondyrev and D. A. Fomina, J. Russ. Phys. Chem. Soc., 47, 190 (1915).

[8] H. Gilman, J. Am. Chem. Soc., 46, 2823 (1924); 61, 957 (1938).

[9] M. S. Kharash, J. Am. Chem. Soc., 52, 2919 (1930).

[10] Champetier, Bull. Soc. Chim., 4, 47, 1131 (1930).

[11] G. Natta, La Chim. et l'Ind., 2, 124 (1956).

[12] V. Grignard, Ann. Chim., 7, 24, 441 (1901).

Institute of High-Molecular Compounds
of the Academy of Sciences of the USSR

Received March 22, 1957

BLANK
PAGE

THERMAL TELOMERIZATION OF OLEFINS WITH SILANES CONTAINING Si-H BOND

Academician A. N. Nesmeyanov, R. Kh. Freidlina and E. Ts. Chukovskaya

As we showed earlier [1], ethylene enters into a telomerization reaction with methyldichlorosilane and trichlorosilane at a temperature of 270-300° under pressure in conditions ensuring an excess of ethylene, and gives a mixture of substances of the structure $XSiCl_2(CH_2CH_2)_nH$ where X = Cl, CH_3. The reaction was conducted in steel autoclaves without addition of a catalyst or reaction initiator. Propylene likewise readily enters into a telomerization reaction with methyldichlorosilane under these conditions.

It appeared of interest to establish whether this reaction could take place with silanes not containing halogen as well as silanes in which the silicon was linked to an aromatic nucleus, i.e., whether reactions of the following types were possible:

$$R_3SiH + n\,CH_2{=}CH_2 \rightarrow R_3Si(CH_2CH_2)_nH,$$

where R = Alk; OAlk:

$$ArSiCl_2H + n\,CH_2{=}CH_2 \rightarrow ArSiCl_2(CH_2CH_2)_nH.$$

In the literature on the addition of silanes of this type at the double bond of olefins, it is reported that in presence of initiators of radical reactions, triethoxysilane generally does not add on at the double bond, [2]* and that triethylsilane likewise does not react or gives a low yield of impure product [2,4].

Phenyldichlorosilane is reported [5] to react with ethylene at temperatures of 200-550° to form phenylethyldichlorosilane.

We established that ethylene enters smoothly into thermal telomerization reaction with phenyldichlorosilane. At 280° and 90 atm. we obtained a compound with the composition $C_6H_5SiCl_2(CH_2CH_2)_nH$, where n = 1,2,3. The reaction of ethylene with triethylsilane was conducted at 300° and 200 atm. Tetraethylsilane and triethyl-n-butylsilane were isolated from the reaction products. Fractions containing higher triethylalkylsilanes were also obtained.

A pressure drop was also observed in the reaction of triethoxysilane with ethylene at 300° (from 100 to 35 atm.) as well as absorption of ethylene (22 g on 75 g charged triethoxysilane). We were unable, however, to isolate pure alkyltriethoxysilanes because a disproportionation reaction evidently take place under the experimental conditions.

Preparation of the starting silanes. $(C_2H_5)_2SiH$ was prepared from $C_2H_5SiCl_2H$ by the Grignard reaction; b.p. 108-109°; n_D^{20} 1.4115. Literature data: b.p. 107° [6]; 103.5-104.5° [7]; n_D^{20} 1.4117 [6]; n_D^{20} 1.4100 [7].

Triethoxysilane was synthesized by the method of Havill et al., [8]. The constants of the preparation agreed with the literature data.

Phenyldichlorosilane was synthesized from silicochloroform and phenylmagnesium bromide [9]. The constants agreed with those in the literature.

* According to patent data [3] triethoxysilane reacts with ethylene in presence of platinized asbestos to give a 50% yield of ethyltriethoxysilane.

Telomerization of ethylene with triethylsilane. The reaction was carried out in a 0.5-liter steel autoclave. 90 g of $(C_2H_5)_3SiH$ was charged into the autoclave, nitrogen was passed through and then ethylene was introduced. The reaction mixture was heated to 300°, the pressure rising at the same time to 200 atm. Reaction was effected at 300-310° for 4 hours. During the process the ethylene pressure fell to 80 atm. Weight of reaction product 119 g. It was fractionated in a column with 15 theoretical plates to give:

a) 60 g of original triethylsilane, b.p. 105-109°; n_D^{20} 1.4112.

b) 15 g tetraethylsilane, b.p. 153°; n_D^{20} 1.4246; d_4^{20} 0.7665; MR_{found} 48.30; $MR_{calcd.}$ 48.78.

Found %: C 66.82, 66.59; H 13.96, 13.92. $C_8H_{20}Si$. Calculated %: C 66.56; H 13.97.

Literature data [10]: b.p. 153°; d_4^{20} 0.7662; n_D^{25} 1.4240.

c) 8 g of triethylbutylsilane, b.p. 89-93°/30 mm; n_D^{20} 1.4360; d_4^{20} 0.7810; MR_{found} 57.60; $MR_{calcd.}$ 58.08.

Found %: C 70.37, 70.31; H 14.08, 14.08; Si 15.57, 15.57. $C_{10}H_{24}Si$. Calculated %: C 70.24; H 14.03; Si 15.66.

Literature data [10]: b.p. 192°; n_D^{25} 1.4358; d_4^{20} 0.7786

d) 18.5 g of 70-110°/4 mm fraction. We failed to isolate hexyl- and octyltriethylsilanes from it in the pure form, evidently due to the presence of traces of products of a disproportionation reaction. Residue 11 g.

Telomerization of ethylene with phenyldichlorosilane. The reaction was carried out in a 0.15-liter autoclave of EYa-1T steel. Into this was charged 35 g of $C_6H_5SiCl_2H$, and ethylene was introduced after passage of a stream of nitrogen. The reaction mixture was heated to 280°, the pressure rising to 90 atm. Reaction was effected at 280-300° for 3 hours and the pressure dropped to 60 atm. 43 g of product was obtained. This was fractionated in a column of 15 theoretical plates to give the following fractions:

Fraction I: b.p. 104-107°/20 mm, weight 14 g, n_D^{20} 1.5170

Fraction II: b.p. 78-83°/2 mm, weight 4.7 g, n_D^{20} 1.5140

Fraction III: b.p. 98-104°/3 mm, weight 3 g, n_D^{20} 1.5100.

Residue 11 g.

Redistillation gave pure fractions of phenylethyldichlorosilane, phenylbutyldichlorosilane and phenylhexyldichlorosilane from fractions I, II and III respectively. These compounds rapidly turn red in light and readily hydrolyze in the air. Properties and analyses of the compounds are presented in Table 1.

TABLE 1

Analysis and Physical Constants of $C_6H_5SiCl_2(CH_2CH_2)_nH$

n	n_D^{20}	d_4^{20}	MR found	MR calc.	B. p., °C/mm	C, % calc.	C, % found	H, % calc.	H, % found	Si, % calc.	Si, % found	Cl, % calc.	Cl, % found
1*	1.5180	1.1490	54.12	54.12	84/7	46.83	47.17 47.18	4.89	4.98 5.18	13.62	13.63 13.24	34.66	34.64 34.09
2	1.5140	1.1151	62.80	63.42	90–91/3	51.49	51.11 50.94	6.05	6.10 6.26	30.41	30.14 30.78	12.05	12.05 11.68
3	1.5100	1.0832	72.15	72.72	115–118/3	55.12	55.17 55.26	7.07	6.90 7.13	27.13	26.94 27.08	10.75	10.83 10.38

* Literature data: b.p. 134-135.5°/5 mm [4], 225-235° [12].

LITERATURE CITED

[1] A. N. Nesmeyanov, R. Kh. Freidlina and E. Ts. Chukovskaya, Proc. Acad. Sci. USSR, 112, 271 (1957); 113, 120 (1957).*

[2] E. Pletrutza, L. Sommer and F. Whitmore, J. Am. Chem. Soc., 70, 484 (1948).

[3] G. Wagner and C. Strother, British Patent 670617.

[4] D. Seyferth and E. Rochow, J. Org. Chem., 20, 250 (1955).

[5] A. J. Barry, D. E. Hook and I. DePree, U. S. Patent 2510853; Chem. Abstr., 44, 8933 c (1950); British Patent 632824, Chem. Abstr., 44, 5378 (1950).

[6] F. Whitmore, E. Pletrutza and L. Sommer, J. Am. Chem. Soc., 69, 2108 (1947).

[7] H. Gilman, R. Ingham and A. Smith, J. Org. Chem., 18, 1743 (1953).

[8] M. Havill, J. Joffe, and H. Post, J. Org. Chem., 13, 280 (1948).

[9] A. J. Barry, British Patent 618403; Chem. Abstr., 43, 5801 (1949).

[10] F. Whitmore and L. Sommer, et al., J. Am. Chem. Soc., 68, 475 (1946).

[11] R. F. Flemming, United States Patent 2386452; Chem. Abstr., 40, 6039 (1946).

Institute of Heteroorganic Compounds
of the Academy of Sciences of the USSR

Received July 5, 1957

*Original Russian pagination. See C.B. Translation.

BLANK
PAGE

THE ASSOCIATION OF ORGANOLITHIUM COMPOUNDS OF THE ALIPHATIC SERIES IN HYDROCARBON SOLUTIONS

K. B. Piotrovsky and M. P. Ronina

(Presented by Academician A. N. Nesmeyanov, April 10, 1957)

In the determination of the molecular weight of phenyllithium and benzyllithium in ethereal solutions by the ebullioscopic method, Wittig, Meyer and Lange [1] found that these compounds form "autocomplexes" of the general formula:

$$[LiR_2]^-Li^+.$$

Our objective was to establish whether organolithium compounds of the aliphatic series were susceptible to similar complex formation in solutions of hydrocarbons. For this purpose we determined the molecular weight of ethyllithium and butyllithium by the cryoscopic method. As solvents we made use of benzene and cyclohexane of the degree of purity specified for these solvents in cryoscopic measurements. Ethyllithium and butyllithium were synthesized in the same solvents by the known procedure based on interaction of the corresponding chloro derivative with metallic lithium [2].

TABLE 1

Data for Determination of Molecular Weight of Ethyllithium in Benzene

Amount of benzene, ml	Amount of LiC_2H_5 introduced (moles)	Molar concentration of LiC_2H_5 per 1000 g benzene	Experiment 1		Experiment 2	
			depression, °C	M found for LiC_2H_5	depression, °C	M found for LiC_2H_5
31.9	0.001178	0.042	0.11	68.4	0.10	77.0
32.9	0.001698	0.059	0.17	63.3	0.15	71.8
34.4	0.002728	0.091	0.24	68.9	0.22	76.8
36.5	0.004030	0.126	0.34	67.7	0.33	70.0
40.2	0.006324	0.180	0.50	65.6	0.49	65.3
47.5	0.010850	0.261	0.72	66.2	0.70	68.7
55.0	0.015500	0.313	0.87	67.6	0.87	67.6
69	0.024180	0.401	0.96	76.1	1.01	70.9
75	0.027900	0.425	0.99	78.3	—	—

After performance of the synthesis, the solutions of ethyllithium and butyllithium were transferred (in a stream of oxygen-free nitrogen) into a Schlenk vessel fitted with a measuring buret (graduated in 0.1 ml) and taps. The concentration of organolithium compounds in solution was determined by double titration [3]. In special determinations it was established that lithium chloride is substantially absent from benzene solutions of ethyllithium and butyllithium, and its content did not exceed 0.1-0.5 weight-% calculated on the organolithium compound.

Use was made in the investigation of solutions having a normality of approx. 0.6 for ethyllithium and 0.6-0.8 for butyllithium. Bearing in mind the great sensitivity of organolithium compounds towards moisture and oxygen, we carried out all of the cryoscopic determinations in a special cryoscope excluding contact of the solutions with the external atmosphere. The cryscope had a ground-glass stopper and a Beckmann thermometer (graduated in 0.01°) and was equipped with two taps which served for introduction of the solutions of organolithium compounds under a nitrogen stream. The cryoscope was placed in a glass air-jacket and the whole set-up was kept throughout the period of measurements in a Dewar vessel in which a temperature of +1° was maintained. The solution was stirred by an electromagnetic stirrer. Before the start of a determination, the cryoscope was subjected to careful preliminary treatment for removal of gases and vapors occluded by the glass. This was done by prolonged pumping out of the apparatus in vacuum while heating and subsequent purging with nitrogen freed of oxygen and moisture.

TABLE 2

Data for Determination of Molecular Weight of Butyllithium in Benzene

Amount of benzene, ml	Moles of LiC_4H_9 introduced	Molar concentration of LiC_4H_9 per 1000 g benzene	Experiment 1		Experiment 2	
			depression, °C	M found for LiC_4H_9	Depression, °C	M found for LiC_4H_9
31.0	0.00068	0.032	0.08	131.7	0.08	131.7
32.5	0.00220	0.077	0.19	132.2	0.20	125.8
34.0	0.00352	0.118	0.26	147.7	0.28	137.0
35.0	0.00528	0.168	0.37	147.1	0.40	135.1
39.0	0.00792	0.227	0.51	147.8	0.53	142.3
42.0	0.01056	0.287	0.63	148.4	0.66	141.3
45.0	0.01320	0.335	0.73	149.1	0.75	142.5
48.0	0.01584	0.377	0.83	147.5	0.87	140.9
58.0	0.02464	0.486	1.07	147.3	1.08	149.3
68.0	0.03344	0.562	1.22	149.3	1.23	149.0

Into the so-prepared cryoscope was admitted 30 ml of solvent (to an accuracy of 0.1 ml) from the Schlenk vessel in which the carefully purified solvent had been kept over sodium wire.

After the freezing point of the pure solvent in the cryoscope had been determined, the solution of organolithium compound was admitted from a Schlenk vessel (in the same solvent) in a nitrogen stream in quantities ensuring formation of a given concentration of organolithium compound for determination of the molecular weight.

TABLE 3

Data for Determination of Molecular Weight of Butyllithium in Cyclohexane

Amount of benzene, ml	Moles of LiC_4H_9 introduced	Molar concentration of LiC_4H_9 per 1000 g cyclohexane	Experiment 1		Experiment 2	
			depression, °C	M found for LiC_4H_9	depression, °C	M found for LiC_4H_9
31.0	0.00081	0.032	0.26	167.4	0.29	150.1
32.5	0.00203	0.080	0.59	175.2	0.62	167.1
34.0	0.00324	0.123	0.93	170.6	0.90	176.4
36.0	0.00486	0.174	1.32	170.3	1.28	175.6
39.0	0.00729	0.241	1.81	172.0	1.80	173.0
42.0	0.00972	0.298	2.24	172.0	2.19	176.0
45.0	0.01215	0.348	2.66	169.1	2.63	171.0

After the conclusion of this operation, the freezing point of the solution of organolithium compound of the given concentration was determined, the cryoscope was withdrawn from the Dewar vessel, and into it was charged a supplementary amount of solution of alkyllithium. In this manner, the total quantity of solvent was steadily increased as the experiment progressed, and this was taken into account for calculation of the molecular weight. At the end of the experiment, the quantity of organolithium compound was determined [3]; in all cases this was 99-99.5% of that admitted during the determination. The molecular weight was calculated from the generally accepted formula: $M = \frac{E \cdot c \cdot 1000}{L \cdot d \cdot \Delta}$. The cryoscopic constant for benzene was taken (in agreement with the literature) to be 5.07, and that for cyclohexane was taken to be 20.2. The specific gravities of the benzene and cyclohexane used in the work were determined at 0.875 and 0.777 respectively. Results of molecular weight determinations of ethyllithium in benzene and of butyllithium in benzene and cyclohexane are given in Table 1-3.

The tabulated data show that ethyllithium is in the associated state in benzene in the concentration range of 0.04-0.4 mole per 1000 g solvent. The experimentally found molecular weight is substantially double the calculated value. Butyllithium in benzene (concentrations of 0.03-0.55 mole per 1000 g solvent) and cyclohexane (0.03 to 0.35 mole per 100 g solvent) is also associated, but the experimental value of the molecular weight of butyllithium is rather more than twice the calculated molecular weight.

Consequently, the present investigation has shown that organolithium compounds of the aliphatic series are in the associated (dimeric) state in solutions in hydrocarbons.

LITERATURE CITED

[1] G. Wittig, F. J. Meyer and G. Lange, Lieb. Ann. 571, 167 (1951).

[2] K. A. Kocheshkov and T. V. Talalaeva, Synthetic methods in the field of organometallic compounds of lithium, sodium, potassium, rubidium and cesium, Acad. Sci. USSR Press, 1949, p. 28.

[3] H. Gilman and A. H. Haubein, J. Am. Chem. Soc., 66, 1515 (1944).

S. V. Lebedev Insitutute of Synthetic Rubber Research

Received April 10, 1957

BLANK
PAGE

THE CHEMICAL COMPOSITION OF GASOLINES FROM THERMAL AND CATALYTIC CRACKING*

Academician A. V. Topchiev, I. A. Musaev and G. D. Galpern

Knowledge of the nature of the unsaturated and other groups of hydrocarbons entering into the composition of cracking products is of great interest. Not enough is known as yet about the influence of the chemical composition of the feedstocks for various thermal treatment processes on the composition and structure of the unsaturated and other groups of hydrocarbons formed in such processes. Solution of this problem would enable us to make a rational choice of raw material for production of light petroleum products with specific qualities and would open up a number of possibilities for petroleum chemical synthesis. Certain difficulties are encountered in the investigation of the composition of cracking products.

A combination method for investigation of the exact chemical composition of cracking gasolines was first proposed by N. D. Zelinsky, and R. Ya. Levina. This was a combination of sulfuric acid treatment with catalytic hydrogenation and dehydrogenation [1,3].

We suggested the use of a copper catalyst [4-6] for selective hydrogenation of unsaturated hydrocarbons under hydrogen pressure in presence of aromatics (free of sulfur compounds). Glushnev and Nepryakhina later applied this method to the investigation of the chemical composition of gasolines from oxidative cracking [7, 8].

G. M. Mamedaliev [9] suggested the use of nickel-on-kieselguhr as catalyst for the above purpose. Hydrogenation of unsaturated compounds was conducted at atmospheric pressure and various temperatures (depending upon the boiling point of the fraction).

In the present investigation we used a combination method comprising: 1) the sulfuric acid method of determination of the overall content of unsaturated and aromatic compounds (sulfonation was effected with Kattwinkel's solution (30 g P_2O_5 + 100 ml H_2SO_4, d = 1.84) cooled with iced water; 2) determination of the percent content of unsaturated hydrocarbons in the fractions by the iodine number and molecular weight; 3) selective hydrogenation of unsaturated hydrocarbons at a pressure of 80 atm. hydrogen and at 280-300° in a laboratory set-up using an experimental autoclave (10); 4) catalytic dehydrogenation for establishment of the nature of the cyclanes (both saturated and unsaturated); 5) the aniline point method for determination of the group composition of the fractions not containing unsaturates. The present work was carried out on distillates from thermal and catalytic cracking obtained from the same Grozny paraffinic petroleum at the Grozny Petroleum Refinery.

Iodine numbers were determined in all cases by the Kaufmann-Galpern method [11].

Investigation of gasoline from thermal cracking. The works gasoline was dried and fractionated in a column with an efficiency of 30 theoretical plates in a weak nitrogen stream.

Yields and characteristics of the fractions are presented in Table 1. 605 g of material was subjected to fractional distillation.

The fractions were divided into two parts for examination; one part was investigated by the sulfuric acid method; the second part was first subjected to selective hydrogenation of unsaturates over copper catalyst. After sulfonation and distillation from polymers, the naphthene-paraffinic residue was subjected to exhaustive dehydrogenation over platinum-iron catalyst [12] prepared by the method described [13].

*The experimental work was carried out with participation of E.G. Iskhakova, T.V. Fedorova, T.N. Buturlova and N.N. Chekalova.

TABLE 1

Fraction No.	Temperature °C	Yield, % paraffins	Yield, % %	n_D^{20}	d_4^{20}	Aniline point$_{max}$	Iodine number	Mol. weight$_{mean}$
0	23—60	31.7	5.3	1.3740	0.6512	51.5	163.2	—
1	60—95	66.3	10.9	1.4038	0.7089	41.5	134.5	91.0
2	95—122	74.3	12.3	1.4200	0.7475	40.9	120.1	105.0
3	122—150	85.5	14.1	1.4330	0.7709	42.5	97.9	116.0
4	150—200	144.5	23.6	1.4505	0.8044	46.5	70.9	144.0
5	Above 200	181.0	29.9	—	—	—	—	—
6	Losses	21.9	3.9	—	—	—	—	—
	Total	605.0	100.0					

TABLE 2

Fraction No.	Temperature °C	Yield, %	Unsaturated: hexamethyl	Unsaturated: pentamethyl	Unsaturated: aromatic	Unsaturated: acyclic	Saturated: aromatic	Saturated: hexamethyl	Saturated: pentamethyl	Saturated: paraffins
1	60—95	18	4.6 0.8	11.8 2.1	—	34.1 6.1	4.7 0.8	5.1 0.9	5.9 1.1	33.8 6.1
2	95—122	20	7.2 1.4	16.7 3.3	1.2 0.2	24.5 4.9	9.3 1.9	10.4 2.1	6.4 1.3	24.3 4.8
3	122—150	23	8.3 1.9	13.0 3.0	2.3 0.5	21.3 4.9	13.3 3.0	8.7 2.0	7.4 1.7	25.7 5.9
4	150—200	39	8.1 3.1	9.0 3.5	1.8 0.7	21.4 8.3	13.9 5.4	8.8 3.4	6.4 2.5	30.6 11.9

Note: Above the line is the content of hydrocarbons in weight-%; below the line in weight-% calculated on the total 60-200° gasoline.

TABLE 3

Fraction No.	Temperature, °C	Yield g	Yield %	n_D^{20}	d_4^{20}	Aniline point$_{max}$	Iodine number	Mol. wt.$_{mean}$
0	To 60	249.3	19.8	1.3649	0.6383	46.0	30.2	—
1	60—95	222.5	17.7	1.3990	0.7094	51.0	33.9	98.3
2	95—122	125.8	9.9	1.4249	0.7592	41.8	28.7	99.6
3	122—150	130.0	10.5	1.4499	0.7978	26.5	17.0	103.2
4	150—200	258.0	20.4	1.4709	0.8324	24.5	13.0	140.7
5	Above 200	254.0	20.1	—	—	—	—	—
6	Losses	22.4	1.8	—	—	—	—	—
	Total ...	1262.0	100.0					

The content of aromatics (primary), hexamethylenic (after dehydrogenation) and pentamethylenic hydrocarbons was determined by the aniline method; the content of paraffins was determined by difference.

In Table 2 are given the final data for the content of hydrocarbons of different groups in gasoline from thermal cracking in standard fractions and recalculated for the whole gasoline (60-200°).

Investigation of a gasoline from catalytic cracking. A similar method was used. Characteristics of the starting fractions are shown in Table 3 (1202 g was fractionated).

The detailed group-chemical composition of a gasoline from catalytic cracking (60-200°) and its fractions was determined on the basis of the sulfuric acid-aniline method of selective hydrogenation of unsaturated hydrocarbons and of dehydrogenation of six-membered naphthenes. The final results are presented in Table 4.

The combination method was applied to the examination of the precise group composition of gasolines from thermal and catalytic cracking obtained from one and the same paraffinic Grozny petroleum. It was shown that a high content of unsaturated hydrocarbons (44.7%) with predominance of acyclic members (24.2%) is characteristic of 60-200° fractions of gasoline from thermal cracking. An appreciable concentration of unsaturated hydrocarbons of the cyclohexene series (7.2%) and of cyclopentenes (11.9%) was found.

TABLE 4

Fraction No.	Temperature °C	Yield, %	Unsaturated				Saturated			
			hexamethyl	pentamethyl	aromatic	acyclic	aromatic	hexamethyl	pentamethyl	paraffins
1	60–95	30	0.4	6.5	—	9.1	5.1	4.7	18.3	35.9
			0.1	1.9		2.7	1.5	1.4	5.5	10.8
2	95–122	17	—	7.0	2.5	3.3	16.5	16.8	15.0	38.9
				1.2	0.4	0.5	2.8	2.9	2.6	6.6
3	122–150	18	—	5.3	—	6.3	42.6	12.7	7.7	25.4
				1.0		1.1	7.7	2.3	1.4	4.5
4	150–200	35	2.0	1.2	0.7	3.1	60.3	6.8	4.4	21.5
			0.7	0.4	0.2	1.1	21.1	2.4	1.5	7.5

Note: Above the line is the content of hydrocarbons in weight-%; below the line is the weight-% of the entire 60-200° gasoline.

The relatively high content of paraffins (28.8%) in all of the fractions is close to the content of acyclic unsaturates. Examination in similar fashion of a gasoline from catalytic cracking showed the following characteristics: low content of unsaturated hydrocarbons, represented by nearly equal amounts by acyclic (5.4%) compounds and compounds with a five-membered ring (4.5%), with nearly complete absence of unsaturates with a six-membered ring (0.8%). The content of paraffinic hydrocarbons considerably exceeds the content of olefins; the content of aromatic hydrocarbons rises rapidly with increasing distillation temperature and reaches 60% for the 150-200° fraction.

Both of the investigated gasolines were free of dienic hydrocarbons with a conjugated bond. Studies by the combination method of the group and individual hydrocarbon compositions of cracking products are being continued.

LITERATURE CITED

[1] N. D. Zelinsky and R. Ya. Levina, J. Appl. Chem., 6, 20 (1933).

[2] N. D. Zelinsky and R. Ya. Levina, Pet. Ind. No. 9, 47 (1934).

[3] R. Ya. Levina, Sci. Memoirs Moscow State Univ., No. 3, Chemistry, 241 (1934).

[4] I. A. Musaev and G. D. Galpern, J. Appl. Chem., 7, No. 4, 572 (1939).

[5] I. A. Musaev, Proc. Acad. Sci. USSR, 13, No. 6, 1097 (1949).

[6] I. A. Musaev, Proc. Acad. Sci. USSR, 80, No. 5, 759 (1951).

[7] V. E. Glushnev and A. V. Nepryakhina, Trans. Inst. Pet. Acad. Sci. USSR, 4, 31 (1954).

[8] V. E. Glushnev and A. V. Nepryakhina, loc. cit., 4, 38 (1954).

[9] G. M. Mamedaliev and Kh. D. Rzaeva, Bull. Acad. Sci. Azerbaijan SSR, No. 7, 3 (1952).

[10] I. A. Musaev and G. D. Galpern, Trans. Inst. Pet. Acad. Sci. USSR, 1, 244 (1950).

[11] G. D. Galpern, Trans. Inst. Pet. Acad. Sci. USSR, 4, 116 (1954).

[12] B. A. Kazansky and G. S. Landsberg, Determination of the individual composition of straight-run gasolines (Instruction). Inst. Org. Chem. Acad. Sci. USSR, 1951 (funds).

[13] I. A. Musaev and G. D. Galpern, Proc. Acad. Sci. USSR, 88, No. 1, 71 (1953).

Institute of Petroleum of the Academy of Sciences of the USSR

Received July 9, 1956

THE MECHANISM FOR THE OXIMATION OF CYCLOHEXANONE WITH SODIUM HYDROXYLAMINE MONOSULFONATE

E. N. Zilberman and M. M. Smirnova

(Presented by Academician B. A. Kazansky, May 15, 1957)

It is customary to use hydroxylamine salts for the oximation of aldehydes and ketones. However, in industry [1] for the oximation of cyclohexanone at times, instead of a hydroxylamine salt, an acid solution of the hydroxylamine monosulfonate – the intermediate product in the synthesis of hydroxylamine sulfate by the Raschig method [2] – is used.

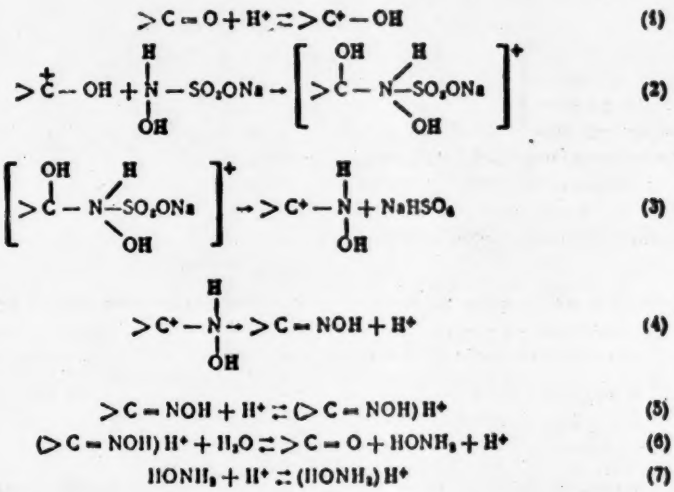
The mechanism for oximation with hydroxylamine monosulfonates is not described in the literature. To react cyclohexanone with sodium hydroxylamine monosulfonate the following is characteristic:

1) In contrast to hydroxylamine, the hydroxylamine monosulfonate does not react with cyclohexanone in alkaline medium.

2) For all practical purposes the hydroxylamine monosulfonate does not hydrolyze at room temperature in dilute sulfuric acid solutions (i.e., under the experimental conditions used by us).

3) In the mutual presence of cyclohexanone and acid the hydroxylamine monosulfonate reacts with ease to give cyclohexanone oxime and also hydroxylamine.

To explain the peculiarities of reacting sodium hydroxylamine monosulfonate with cyclohexanone in acid medium we proposed the following reaction scheme:



(1)

(2)

(3)

(4)

(5)

(6)

(7)

In accord with the proposed mechanism the first reaction product is the carbonium ion, which then forms a coordination bond due to the unshared electron pair of the nitrogen atom in the nucleophilic hydroxylamine monosulfonate. Then a molecule of bisulfate and a proton are cleaved from the complex formed in this manner and the oxime is formed. In acid medium the equilibrium hydrolysis of the oxime is established, leading to the formation of the original ketone and the hydroxylamine salt. In the described scheme the most rapid reactions are (3) and (4). The rate of decrease in the concentration of the hydroxylamine monosulfonate (or oximation rate of the ketone) should first of all depend on the bimolecular reactions (1) and (2), i.e., on the concentrations of the ketone, the hydrogen ions and the hydroxylamine monosulfonate. The presence of hydrogen ions determines the hydrolysis of the cyclohexanone oxime to yield cyclohexanone and hydroxylammonium ion, and consequently the secondary reactions (5)-(7) also exert an influence on the macrokinetics of the whole process.

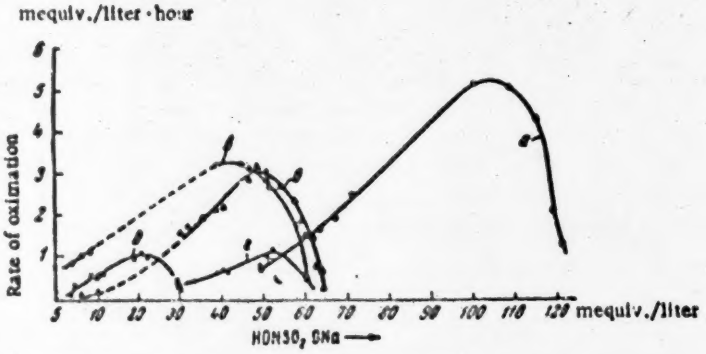


Fig. 1. Oximation of cyclohexanone with sodium hydroxylamine monosulfonate at 22°. Original solutions (in mequiv./liter):

	$HONHSO_2Na$	$C_6H_{10}O$
a	124	62
b	64.8	65
c	62	124
d	62	31
e	31	62

The reaction scheme depicted above was confirmed by the kinetics data obtained for the oximation of cyclohexanone with sodium hydroxylamine monosulfonate. From Fig. 1 it can be seen, with other conditions constant, that the oximation rate increases with increase in the original cyclohexanone concentration. The influence of the hydroxylamine monosulfonate concentration on the reaction rate obeys the same rule. In all of the experiments, shown in Fig. 1, the reaction is self-accelerating in the initial period of reaction between the starting substances. In addition, from the slope of the curves in these plots it follows that the greater the concentration of either the ketone or the hydroxylamine monosulfonate, the more rapid is the increase in the reaction rate.

This leads us to postulate that the autocatalytic nature of the process is determined by an increase in the concentration of one of the reaction products of the hydroxylamine monosulfonate with cyclohexanone. From the experiments it can be seen that the acidity of the system increases during the course of reaction.

However, a part of the formed protons should react with the oxime and hydroxylamine, as a result of which only the free hydrogen ions can exert an influence on the oximation rate, i.e., the studied reaction apparently represents a case of specific acidic catalysis.

To verify further the mechanism proposed by us for the reaction of cyclohexanone with the hydroxylamine monosulfonate in acid medium we ran some experiments to determine the order of the reaction. We judged

by the increase in the total acidity of the system in calculating the velocity constants relative to the hydroxylamine monosulfonate concentration (C_1) and relative to the oximation rate. The amount of cyclohexanone (C_2) in the reaction mixture at the start of experiment (i.e., when a large excess of cyclohexanone with respect to the cyclohexanone oxime was present, making it possible to neglect the hydrolysis of the oxime) was calculated from the increase in the total acidity, in the same manner as the hydroxylamine monosulfonate concentration was calculated. In subsequent determinations the amount of cyclohexanone, formed in the hydrolysis of the oxime, was also taken into account. For this we used the equilibrium constants [3] of reaction (6), making the tentative assumption that the equilibrium state had been reached in this reaction. The hydrogen ion concentration (C_3) was calculated from the pH of the medium. The experimental data (total acidity and hydrogen ion concentration) are plotted in Fig. 2.

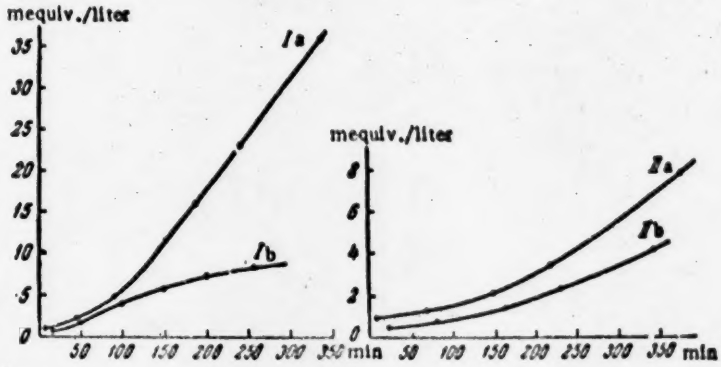


Fig. 2. Oximation of cyclohexanone (I) 95.6, (II) 62 mequiv./liter) with sodium hydroxylamine monosulfonate (I) 96, (II) 62 mequiv./liter). a) Total acidity; b) hydrogen ion concentration.

TABLE 1

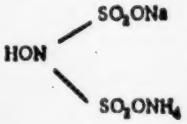
Calculation of the Velocity Constants for the Oximation of Cyclohexanone with Sodium Hydroxylamine Monosulfonate at 22°

Time, min.	Total acidity, mequiv/liter	Concentration of the components, mequiv./liter C_1	C_2	C_3	Velocity, mequiv/liter·hr	Velocity constant $k \cdot 10^4$
4	0.88					
24		94.6	94.2	1.02	1.61	1.77
44	1.95					
67		92.8	92.4	2.40	3.23	1.55
91	4.48					
141		86.1	87.2	5.37	6.54	1.63
191	15.4					
217		76.9	80.0	7.6	8.5	1.83
243	22.8					
293		66.8	75.1	8.5	7.6	1.77
343	35.5					
					Average	1.71

On the basis of the data in Fig. 2 we calculated (Table 1) by means of the equation for third order reactions $V = kC_1C_2C_3$ that the average velocity constant was equal to $1.7 \cdot 10^{-4}$ liter^3/hour·mequiv^3. We were unable to obtain any concordant results for the velocity constant if we neglected the participation of hydrogen ions in the reaction. As a result, the oximation rate changes proportionally to the sodium hydroxylamine monosulfonate, cyclohexanone and hydrogen ion concentrations, which is in agreement with the reaction scheme proposed in this paper.

EXPERIMENTAL

To synthesize sodium hydroxylamine monosulfonate we took 500 ml of technical hydroxylamine disul-



fonate solution, concentration of 396 g/liter, obtained from sodium nitrite, ammonium

bisulfate and sulfur dioxide, and added to it 61 ml. of 40% NaOH to remove ammonia and then 250 ml of methanol to precipitate the sodium hydroxylamine disulfonate. The obtained precipitate was reprecipitated twice from 9% NaOH solution with methyl alcohol. Subsequent treatment of the sodium hydroxylamine disulfonate was made in accord with the directions of Nast and coworkers [4] for the preparation of potassium hydroxylamine monosulfonate. The yield of sodium hydroxylamine monosulfonate (purity 98-100%) was 10-20 g.

Commercial cyclohexanone was purified through the bisulfite compound; the obtained product had d_4^{20} 0.9454, n_D^{20} 1.4495.

The experiments were run at 22 ± 0.05°. The initial acidity of the reaction mixtures corresponded to pH 3.6-3.2. To determine the total acidity, samples were removed at periodic intervals and titrated with 0.01N NaOH to phenolphthalein. An LP-5 lamp potentiometer with glass electrode was used to measure the pH.

We wish to thank Prof. G. A. Razuvaev for his valuable counsel and the interest shown in our work.

LITERATURE CITED

[1] E. N. Zilberman, Chem. Ind., USSR, No. 5, 277 (1955).

[2] F. Raschig, Schwefel und Stickstoffstudien, Leipzig – Berlin, 1924.

[3] Z. Vodrazka, Chem. listy, 47, No. 7, 996 (1953).

[4] R. Nast, K. Nyul and E. Grziwok, Zs. anorg. allgem. Chemie, 267, 304 (1952).

Received July 19, 1956

STUDY OF THE NITRATION OF ISOPROPYLCYCLOHEXANE WITH NITRIC ACID

Academician A. V. Topchiev, S. D. Mekhtiev and A. Sh. Novruzova

In an earlier paper [1] we gave the main literature references on the nitration of cyclane hydrocarbons, published up to 1948. After this a number of papers were published on the mechanism for the nitration of cyclohexane [2, 4] and on the reaction of cyclohexene with dilute nitric acid [4].

The present paper is devoted to the results obtained by us in studying the nitration of isopropylcyclohexane with nitric acid under various conditions.

EXPERIMENTAL

Starting Raw Materials and Method of Operation. The isopropyl cyclohexane used as starting product for nitration had b.p. 152-154°, d_4 = 0.8006, n_D^{25} 1.4410. As the nitrating agent we used nitric acid with density 1.3, 1.2 and 1.075 (corresponding to a concentration of 48, 28 and 11%, respectively). The nitrations were run in a 500-ml round-bottomed flask, fitted with a ground-glass reflux condenser, through which a thermometer descended into the liquid. A glycerin bath was used to heat the reaction flask.

The calculated amounts of hydrocarbon and nitric acid were placed in the flask. The reaction mixture was heated at a definite temperature for a given length of time. At the end of experiment the upper layer of the reaction mixture, composed of a mixture of nitro product and unreacted hydrocarbon, was washed, dried, and vacuum-distilled through a column. After removing the unreacted starting product the crude nitro product was subjected to fractional distillation through the same column, but at a much lower residual pressure. Then the isolated fractions were analyzed.

To establish the structure of the reaction products a part of the obtained fractions of nitro products were hydrogenated to the corresponding amino derivatives. The reductions were run in an autoclave designed by I. A. Musaeva in the presence of Raney nickel and with high hydrogen pressure. The amino compounds obtained in this manner were then analyzed.

The experiments on the nitration of isopropylcyclohexane were run at 50-55, 80-85 and 105-110°. The duration of experiment was taken as 5, 10, 15 and 20 hours, while the nitric acid concentration was taken as 11% (d = 1.075), 28% (d = 1.2) and 48% (d = 1.3). The molar ratio of hydrocarbon to nitric acid was varied from 1 : 1.25 to 1 : 2.5. A total of more than 40 experiments was run. The results obtained by us in studying the influence of various factors on the nitration process are discussed below.

Influence of Temperature. The results of the experiments in which the nitration was run with acid having d 1.3 and with a 1 : 2.5 molar ratio of hydrocarbon to acid are shown in Fig. 1.

From the character of the curves in Fig. 1A it can be seen that the percent conversion of the starting crude rises sharply with elevation of the reaction temperature, reaching a value of 60.8% at 105°; in this connection an increase in the yields of crude nitro product and mononitro product is observed only up to a temperature of 80°, after which further increase in the temperature leads to a reduction in the yield. Consequently, the optimum reaction temperature for the nitration of isopropylcyclohexane under the conditions of our experiments is 80-85°, and here the yield of the mononitro product is as high as 72.8% of theory (although the percent conversion is only 25.1%). This, evidently, must be explained as being due to the development of oxidation reactions under the given conditions, and also as being due to more profound nitration with the formation of di- and polynitro products.

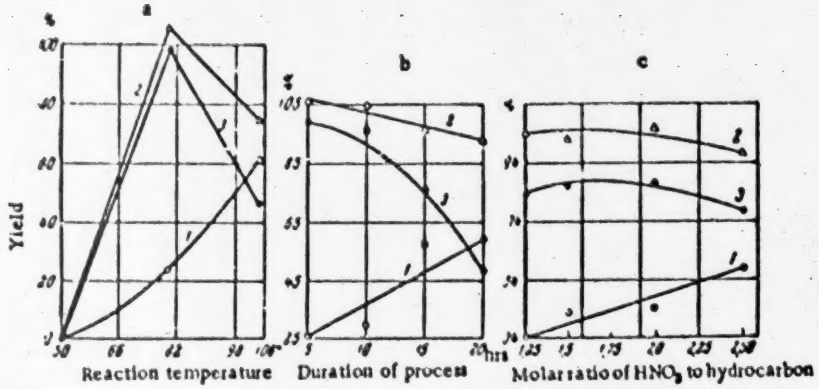


Fig. 1. The nitration of isopropylcyclohexane as a function of the temperature (A), the duration of the process (B), and the relative amount of nitric acid (C): 1) conversion of the hydrocarbon; 2) yield of crude petroleum product in percent on converted hydrocarbon; 3) yield of mononitro compound in percent on converted hydrocarbon.

As a result, in the nitration of cyclanes with nitric acid a change in the reaction temperature influences not only the quantitative side of the conversion, but also to a strong degree determines the direction of the reaction and the nature of the final products.

Influence of the Duration of the Process. In this part of the study we ran a series of experiments on the nitration of isopropylcyclohexane with nitric acid having d 1.3, a temperature of 80-85°, and a molar ratio of hydrocarbon to acid of 1 : 2.5. The time of reaction was taken as 5, 10, 15 and 20 hours. The results of the experiments are shown in Fig. 1B.

An examination of the character of the curves in Fig. 1B shows that under the conditions of our experiments the optimum duration of the nitration reaction is 15 hours. With increase in the duration of the process the specific significance of oxidation reactions increases.

Influence of the Molar Ratio of the Reacting Components. To answer this question we ran a series of experiments on the nitration of isopropylcyclohexane with nitric acid having d 1.3, a temperature of 80-85°, and a reaction time of 15 hours, in which connection the molar ratio of hydrocarbon to nitric acid was varied from 1 : 1.25 to 1 : 2.5. The results of these experiments are shown in Fig. 1C. The character of the curves in Fig. 1C shows that the percent conversion of the starting hydrocarbon decreases with decrease in the relative amount of nitric acid, while the yield of crude nitro product and of mononitro compound in percent on converted crude remains almost constant. As a result, under the conditions of our experiments the optimum molar ratio of hydrocarbon to nitric acid is 1 : 2.5.

Influence of the Nitric Acid Concentration. Our experiments revealed that with the same relative amount of nitric acid the nitration process is strongly dependent on the concentration of the latter. Thus, if nitric acid with d 1.3 is used for nitration, the amount of converted isopropylcyclohexane is 61%, while the yield of crude nitro product and monitro compound (in percent on converted hydrocarbon) is on the average 76.1 and 46.8%, respectively, whereas the use of nitric acid of d 1.075 for the nitration, with other conditions constant and even with a 3-fold increase in the reaction time, leads to the formation of only traces of the nitro product.

In summary, it might be mentioned that the optimum conditions for the nitration of isopropylcyclohexane with nitric acid in the liquid phase are: temperature 80-85°, duration – 15 hours, nitric acid concentration 48% (d = 1.3), and a molar ratio of hydrocarbon to nitric acid equal to 1 : 2.5. Under these conditions the hydrocarbon

conversion is 57%, while the yields of crude nitro product and mononitroisopropylcyclohexane in percent on converted hydrocarbon are 98.3 and 78.6%, respectively.

We are of the opinion that the established dependence of the reaction course for the nitration of isopropylcyclohexane can be explained by the dynamics of the amounts of nitrogen dioxide formed from nitric acid under various conditions, for a reduction in the temperature and a decrease in the reaction time, and also in the concentration and relative amount of nitric acid, lower the capacity of nitric acid to decompose into nitrogen oxides. To verify the latter we ran a special experiment on the nitration of isopropylcyclohexane in the presence of a small amount of ammonium sulfate. For this, a mixture of 43.6 g of isopropylcyclohexane, 9 g of ammonium sulfate and 113.5 g of nitric acid with d 1.3 was heated at 80-85° for 8 hours. Despite the fact that the process was run under conditions proving optimum for the nitration of isopropylcyclohexane, the experiment failed to lead to the formation of even traces of nitro product.

LITERATURE CITED

[1] A. V. Topchiev, Nitration of Hydrocarbons and Other Organic Compounds, Acad. Sci. USSR Press, 1949.*

[2] A. I. Titov and M. K. Matveev, Proc. Acad. Sci. USSR, 83, No. 1, 101 (1952).

[3] A. I. Titov and M. K. Matveeva, J. Gen. Chem., 23, No. 2, 238 (1953).**

[4] A. V. Topchiev and E. A. Fantalova, Proc. Acad. Sci. USSR, 88, No. 1, 82 (1953).

Petroleum Institute
Academy of Sciences of the Azerbaijan SSR

Received July 13, 1956

*In Russian.

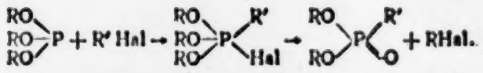
**Original Russian pagination. See C.B. Translation.

BLANK
PAGE

THE REACTION OF THE INTERMEDIATE PRODUCTS OF THE ARBUZOV REARRANGEMENT WITH AMINES

Academician A. E. Arbuzov and N. N. Sazonova

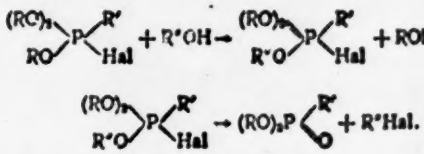
In 1905, one of us discovered the reaction subsequently named the Arbuzov rearrangement. The general scheme of the reaction is:



(1)

For phosphites in which R is an aliphatic radical, the intermediate product is an unstable substance which readily splits out alkyl halide to form an ether of an alkylphosphonic acid. For phosphites in which R is an aromatic radical, the intermediate complex can be isolated in analytically pure form [2,3].

The intermediate products of the Arbuzov rearrangement are reactive substances. They react vigorously with water and various alcohols [2,4]. Landauer and Ridon [4] give the following scheme for reaction of the intermediate complexes with alcohols.



(2)

Since, in all probability, the first stage of the reaction proceeds by means of the hydrogen of the alcohol, a similar reaction might be expected with other substances having an active hydrogen. We used secondary amines in place of alcohol. We prepared the following complexes (No. 1- in Table 1), and reacted them with dialkylamines (diethylamine and dimethylamine).

TABLE 1

Exp. No.	Complex	Conditions: time, hours	Conditions: temp., °C	M.p., °C	Hal, %: calc.	Hal, %: found	Yield, %
1	$(C_6H_5O)_2PCH_2I$	8—10	100	130		25.29	Quant.
2	$(o\text{-}CH_3C_6H_4O)_2PCH_2I$	4	100	135—136	25.7	25.72	Quant.
3	$(o\text{-}ClC_6H_4O)_2PCH_2I$	7	100—110	49	22.86	22.64	75
4	$(p\text{-}ClC_6H_4O)_2PCH_2I$	13	100	104	22.86	22.56	Quant.
5	$(o\text{-}CH_3C_6H_4O)_2PC_2H_5I$	16	110—120	107—108	25	24.84	70
6	$(o\text{-}CH_3C_6H_4O)_2PC_2H_5I$	36	110—120	Oil			

The intermediate products of the Arbuzov rearrangement were prepared by heating equimolar amounts (of phosphite and alkyl halide) in sealed tubes.

First, we decomposed certain of the intermediate complexes with ethyl alcohol, which resulted in the formation of esters of alkylphosphonic acids (Nos. 1-4 in Table 2).

TABLE 2

Exp. No.	Ester	B.p., °C / mm Hg	d_4^{20}	n_D^{20}	P (N), % calc.	P (N), % found	Yield, %	$MR_{calc.}$ / MR_{found}
1	$(o\text{-}CH_3C_6H_4O)_2P(O)CH_3$	215/16	1.1964		11.23	11.08 11.05	74.6	
2	$(o\text{-}CH_3C_6H_4O)_2P(O)C_2H_5$	213—214/12	1.1410	1.5415	10.69	10.48 10.59	38.8	79.75 79.02
3	$(o\text{-}ClC_6H_4O)\text{-}P(O)CH_3$	176—177/3	1.3350	1.5560	9.78	9.9 10.06	30	75.63 76.32
4	$(o\text{-}CH_3C_6H_4O)_2P(O)C_2H_5$	216—217/11	1.1071	1.5321	9.74	9.66 9.78	30,2	88.99 89.02
5	$(C_6H_5O)_2P\text{—}N(C_2H_5)_2$	176—178/4	1.0902	1.5532	10.72	10.74 10.86	62,8	84.85 44

As is well known, the reaction of the intermediate complexes with alcohols is accompanied by the liberation of a large amount of heat. A similar phenomenon was observed during their decomposition with amines.

As a result of the reaction of products 1-5 of Table 1 with amines, phenol or, correspondingly, an analog of it was always formed in quantitative yield. Only in four cases could the second product of this reaction be obtained in the crystalline state and purified by recrystallization from an acetone-ether mixture (Nos. 1-4 in Table 3).

TABLE 3

Exp. No.	Substances	M.p., °C	P, % calc.	P, % found	Yield, %	External form
1	$CH_3(C_6H_4O)_2P{=}\overset{+}{N}(C_2H_5)_3I$	128	7.19	7.08 7.06	56	Needles
2	$CH_3(C_6H_4O)_2P{=}\overset{+}{N}(CH_3)_3I$	008.5 109	7.69	7.58 7.73	28	Needles
3	$CH_3(CH_3C_6H_4O)_2P{=}\overset{+}{N}(C_2H_5)_2I$	141	6.75	6.59 6.54	41.1	Needles
4	$CH_3(CH_3C_6H_4O)_2P{=}\overset{+}{N}(CH_3)_2I$	136.5 137	7.19	7.12 7.26	28.8	Needles

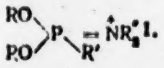
The other products were viscous, light brown liquids which, on standing in air, hydrolyzed with the liberation of the hydriodide of the dialkylamine.

In an attempt to isomerize the ester of diethylamidodiphenylphosphorous acid with methyl iodide, the product obtained was identical to the product of the reaction of methyltriphenylphosphonium iodide with diethyl amine. The amidophosphite (No. 5 in Table 2), a compound with a trivalent phosphorus, violently reacts with bromine in quantitative ratios, and also reacts with cuprous iodide forming a crystalline complex with an m.p. of 111° and a molecular weight of 1443 as against a calculated value of 479.5 × 3 (1438.5).

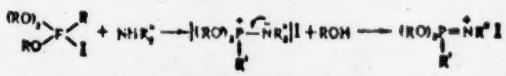
The amidophosphite was prepared from the chloride of diphenylphosphorous acid and diethylamine in an ether medium

$$P(OC_6H_5)_2Cl + 2NH(C_2H_5)_2 = P(OC_6H_5)_2N(C_2H_5)_2 + NH(C_2H_5)_2 \cdot HCl.$$

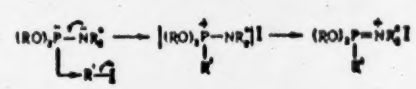
On heating the amidophosphite and methyliodide in equimolar amounts for half an hour at a temperature of 100° and subsequently cooling, the entire mass in the tube completely crystallized. For the basic reaction product we propose the formula:



We propose the following scheme for its formation:



(3)



(4)

In order to confirm the structures proposed for products Nos. 1-4 in Table 3, we carried out a series of chemical reactions.

Saponification of product No. 1 in Table 3 gave methylphosphonic acid with an m.p. of 102° and diethylamine hydriodide in quantitative yields. This fact indicates that the methyl group is bound to the phosphorus.

The iodine in this product was in the form of an ion. This was confirmed by quantitative precipitation of AgI with silver nitrate in an ethyl alcohol medium. Only by such a structure is it possible to explain their non-participation in reactions according to schemes (1) and (2).

The scheme proposed by us for the formation of products Nos. 1-4 of Table 3 finds confirmation in a series of investigations of the isomerization of amidophosphites. It was previously shown by the authors [5-7] that as a result of the isomerization of amidophosphites by alkyl halides, in contrast to the isomerization of diamidophosphites when the normal isomerization product is formed [8], the products obtained were an undistillable oil and a dialkylamine salt.

LITERATURE CITED

[1] A. E. Arbuzov, On the Structure of Phosphorus Acid and Its Derivatives," SPb., 1905.

[2] A. Michaelis and R. Kaehne, Ber., 31, 1048 (1898).

[3] A. E. Arbuzov and I. V. Nesterov, Proc. Acad. Sci. USSR, 92, 57 (1953).

[4] J. Landauer and H. Ridon, J. Chem. Soc., 1958, 2224.

[5] A. E. Arbuzov and V. M. Zoroastrova, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1952, 789.**

[6] B. A. Arbuzov and D. Kh. Yarmukhametova, Proc. Acad. Sci. USSR, 101, 675 (1955).

[7] B. A. Arbuzov, N. I. Rizpolozhensky and M. A. Zvereva, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1955, 1021.**

[8] A. Michaelis, Ann. Chem., 326, 129 (1903).

Received April 29, 1957

*In Russian.

**Original Russian pagination. See C.B. Translation.

BLANK
PAGE

ON THE MECHANISM OF THE THERMAL DECOMPOSITON OF CELLULOSE UNDER VACUUM AND THE FORMATION OF 1,6-ANHYDRO-1,5-GLUCOPYRANOSE– LEVOGLUCOSAN

O. P. Golova, A. M. Pakhomov, E. A. Andrievskaya and R. G. Krylova

(Presented by Academician I. N. Nazarov, June 7, 1957)

Up to the present time, there has been no unequivocal explanation of the mechanism of the formation, during the thermal decomposition of cellulose under vacuum, of 1,6-anhydro-1,5-glucopyranose – levoglucosan – a compound with the elemental composition of a unit of the structural unit of cellulose but having the hydroxyl in a different position (at C_4 instead of C_6) and two oxygen bridges instead of a single 1,5-bridge.

Irvine and Oldham [1] proposed a mechanism for the formation of levoglucosan through an intermediate stage in which the cellulose is hydrolyzed to glucose and dehydration of the latter.

This hypothesis found corroboration in the communications of Karrer [2] on the preparation of levoglucosan in high yields from β-d-glucose.

For an accurate evaluation of the existing ideas on the mechanism of the formation of levoglucosan from cellulose, a part of this mechanism being the thermal depolymerization of polysaccharides to the monomer, we considered it necessary to carry out investigations in order to obtain data for an answer to the questions of the principles connected with the formation of levoglucosan from cellulose.

Such basic data are: 1) obtaining a constant yield of levoglucosan during the thermal decomposition of cellulose, 2) the possibility of the formation of levoglucosan from β-d-glucose, 3) the effect of the physical structure of the cellulose (packing density) on its thermal decomposition, 4) the effect of glucose on the process involved in the formation of levoglucosan from cellulose, and 5) the effect of the degree of polymerization of the cellulose.

As a result of systematic investigations on the effect of changing the various physical factors, conditions were found (temperature, vacuum, and cellulose properties) which give a constant yield of 55-60% levoglucosan.

The results obtained during the study of the possibility of obtaining levoglucosan from β-d-glucose under optimum conditions for the thermal decomposition of cellulose are presented in Table 1. As seen from the data in the table, the yield of levoglucosan comprised only 5-6% of the glucose.

TABLE 1

Production of Levoglucosan from β-d-Glucose and Cellulose During Thermal Decomposition Under Vacuum

Initial material	Yield of products in % of initial material		Yield of levoglucosan in % of initial material
	solid distillate	liquid distillate + dry residue	
β-d-Glucose	39—42	57	5—6
Cellulose	73—75	24	54—60
Levoglucosan	98.8	—	98.8

The investigations of the thermal conversion of glucose show that the conversion of glucose to levoglucosan is possible, but the degree of conversion is very small – only 6%. The data of Karrer showing high yields of levoglucosan from β-d-glucose were not confirmed. The method of separating the products of the thermal decomposition of glucose by means of anion exchange resins, which was first used by us, permitted the identification of levoglucosan and gave unequivocal answers as to the possibility of forming levoglucosan and its amount.

The investigations carried out with celluloses of different structure, as characterized by packing density, were published earlier [3].

The results obtained in that investigation indicate, by means of an actual example, the change in the chemical process in the thermal decomposition of cellulose in relation to packing of the macromolecule. From these data it follows that the chemical processes of the thermal decomposition of cellulose cannot be considered only on the basis of the concept of the structure of the individual polymer molecules. A decrease in the packing density of the macromolecules leads to a decrease in the yield of levoglucosan and increases the yield of products of the deeper decomposition of cellulose.

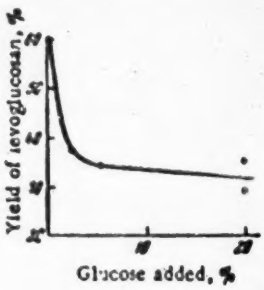


Fig. 1. Effect of adding glucose to cellulose on the yield of levoglucosan.

The facts of the low yield of levoglucosan from β-d-glucose (5-6%) and from easily hydrolyzed cellulose led us to the requirement of an investigation of the effect of the presence of glucose itself on the formation of levoglucosan from cellulose. With this aim, glucose was introduced into the reaction system in amounts of from 2 to 20% of the weight of cellulose. The results are presented in Figure 1.

As seen from Figure 1, the introduction of glucose, regardless of the amount, reduced the yield to 30%.

Since levoglucosan is not the main product of the thermal decomposition of the monomer (glucose), it was necessary also to investigate the effect of the degree of polymerization on the yield of levoglucosan during the thermal decomposition of cellulose. The results of these experiments are presented in Table 2.

TABLE 2

Effect of Degree of Polymerization on the Formation of Levoglucosan

Degree of polymerization	COOH groups per 100 glucose units	Yield of decomposition products, % of cellulose		Levoglucosan content of paste according to increase in R W	Yield of levoglucosan, % of cellulose
		solid distillate	liquid distillate and dry residue		
1000	0.144	78	19.0	77.0	60.0
450	0.144	72	23.0	78.8	56.0
200	0.144	76	22.0	72.0	54.0
190	0.144	74	25.0	72.6	53.0
150	0.144	75	20.0	72.5	54.0
Cellobiose	—	25	—	—	3—4

It follows from the data of Table 2 that a change in the degree of polymerization in the cellulose samples of from 1000 to 150 has practically no effect on the formation of levoglucosan; the yield comprises 55-60% under conditions of constant physical structure.

In order to clarify the question of the minimum chain length in the formation of levoglucosan, an investigation was carried out on the effect of heat and vacuum on cellobiose under the same conditions as in the decomposition of cellulose.

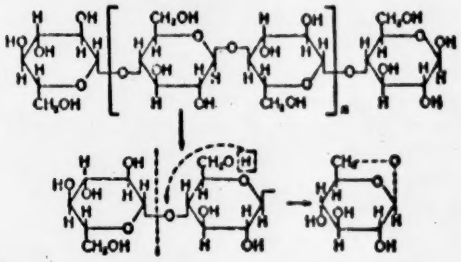
We found that the yield of pasty distillate was 25% and the yield of levoglucosan was only 3-4% calculated on the cellobiose (see Table 2).

Our data show that the basic elements of the hypothesis of the formation of levoglucosan through the intermediate stage of cellulose hydrolysis to glucose and dehydration of the glucose to levoglucosan is not confirmed experimentally and, therefore, that the hypothesis is not correct.

On the basis of these facts, it would be expected that the mechanism of the formation of levoglucosan must include the following processes.

In regions where the packing is dense, the formation of levoglucosan is the primary reaction. Here the processes of dehydration and hydrolysis have only a secondary significance. In regions with a different physical structure, the primary reactions are dehydration and hydrolysis which lead to the formation of chemically changed and, possibly, thermally unstable glucopyranose units of the cellulose molecule. Therefore, in this case the rupture of the 1,4-β-glucosidic bonds does not lead to the formation of levoglucosan.

According to our picture, the process of isomerization apparently includes migration of the hydrogen of the hydroxyl group of the 6th carbon atom to the oxygen atom at the 4th carbon atom and linking of the 1st carbon atom with the 6th through the oxygen atom with the formation of five- and seven-membered rings and with retention of the six-membered ring:



According to the calculation of Reeves [4], the spatial location of the atoms of the anhydroglucose unit favor formation of a 1,6-anhydro ring, since the distance between the 1st and 6th carbon atoms is less than that between any other pair of neighboring carbon atoms.

The decrease in yield of levoglucosan on adding glucose to the cellulose is apparently caused by the inhibiting action of the very active fragments of the glucose molecules on the isomerization of fragments of the cellulose chain to levoglucosan or to the blocking of the radical center which arises as the first act in the process of forming levoglucosan.

It might be supposed that for the formation of significant amounts of levoglucosan through the isomerization of the glucopyranose unit of cellulose, the presence of chains with a high degree of polymerization is required, thereby providing a physical structure which, by blocking the hydroxyl groups through the formation of hydrogen bonds, hinders the process of dehydration and other side reactions.

Conclusions. 1. The low yields of levoglucosan during the thermal decomposition of readily hydrolyzable cellulose, glucose, and cellobiose with the addition of glucose controverts the possible existence of an intermediate stage in which glucose is formed and the dehydration of the glucose to levoglucosan as an intermediate stage in the formation of levoglucosan from cellulose.

These facts do not confirm the hydrolytic-dehydration mechanism of the formation of levoglucosan, a mechanism which is widely cited in the literature.

2. The formation of levoglucosan in considerably yield (55-60%) proceeds only with the presence of a

certain chain length of the cellulose macromolecule. It has been shown that a significant yield of levoglucosan during the thermal decomposition of cellulose under vacuum requires a consolidated cellulose structure.

3. The process of the formation of levoglucosan includes cleavage of the cellulose molecule at the 1,4-β-glucosidic bonds and subsequent isomerization of the resulting chain fragments into levoglucosan molecules.

The basic conclusions made during the investigation of cellulose are perhaps concerned with the occurrence of other polysaccharides during thermal decomposition and also with other forms of polymers.

LITERATURE CITED

[1] I. C. Irvine and J. W. H. Oldham, J. Soc. Chem., Ind., 119, 1744 (1921).

[2] P. Karrer, Helv. Chim. Acta, 3, 258 (1920).

[3] O. P. Golova, A. M. Pakhomov and E. A. Andrievskaya, Proc. Acad. Sci. USSR, 112, No. 3, 430 (1957).*

[4] R. E. Reeve, J. Am. Chem. Soc., 71, 2116 (1949).

N. D. Zelinsky Institute
of Organic Chemistry
Academy of Sciences USSR

Institute of Forests
Academy of Sciences USSR

Received June 28, 1957

*Original Russian pagination. See C.B. Translation.

EXPERIMENTAL BASIS FOR A CHAIN MECHANISM OF THE HETEROGENEOUS-CATALYTIC HYDROPOLYMERIZATION OF OLEFINS UNDER THE INFLUENCE OF CARBON MONOXIDE AND HYDROGEN

N. I. Ershov and Ya. T. Eidus

(Presented by Academician B. A. Kazansky, April 19, 1957)

Chain reactions occurring in space and initiated by free atoms or radicals are widely known and have been studied in detail. However, up to the present time there has been no direct and unequivocal experimental proof of the possibility of the occurrence of a chain process on the surface of a solid catalyst, although it has been shown that certain reactions proceed on a solid catalyst by a chain mechanism, and there has also been published a theoretical work [1] admitting the possibility of chain heterogeneous-catalytic reactions. We have previously shown [2] that radicals formed during the heterogeneous-catalytic reduction of carbon monoxide by hydrogen are initiators for the hydropolymerization of olefins. It was of interest to determine if this is a chain reaction, since in the homogeneous polymerization of olefins under the influence of free atoms and radicals, the process occurs, as a rule, by a chain mechanism. This is true of the polymerization of olefins (ethylene, propylene, butylenes) initiated both by the simplest alkyl radicals (methyl and ethyl) and by methylene radicals obtained by the decomposition of ketene. While carrying out hydropolymerization reactions with C_2-C_4 and C_6 olefins [3-8], it was established that at 190° and atmospheric pressure and with low concentrations of carbon monoxide (1-2%) in approximately equimolar mixtures of olefins and hydrogen, each molecule of carbon monoxide entering into reaction involves up to 45 molecules of olefin (ethylene) in the hydropolymerization process (Figure 1, Curve b). From this it is apparent that, in view of the small quantities of carbon monoxide entering into the reaction, it cannot be considered as a reagent in the usual sense. From its effect on the reaction, which proceeds only with its participation, carbon monoxide must be an initiator of a chain polymerization process or a catalyst. However, the role of a catalyst is excluded in the present case, since carbon monoxide appears in the final product without regeneration. In this reaction, carbon monoxide is an initiator of a process which clearly has some of the basic features which distinguish the chain character of the alkyl free radical-initiated polymerization of olefins in space – the chain length, or yield based on initiator (number of polymerized olefin molecules per initiator particle), significantly exceeds unity, and there is a regular decrease in the length of the chain or initiator yield with an increase in its concentration.

One of the characteristic features of homogeneous chain polymerizations of olefins under the influence of alkyl free radicals is a dependence of chain length or initiator yield on the concentration of these radicals. This dependence is dependent on the difference in the rate of the reaction of the radicals with olefin molecules and that of the recombination of the radicals. With considerable concentrations of radicals, their recombination predominates, and addition to olefins (initiation) proceeds slowly or not at all; on the other hand, with low concentrations of free radicals, conditions are unfavorable for their recombination, and, consequently, there is mass addition to olefins leading to an increase in polymerization rate. Thus, it has been observed that initiator yield increases with decrease in the concentration of initiator (free radicals). All this is readily apparent from the following examples: with the introduction into each 15.3 liters of ethylene of 117, 34, 4, and 0.1 ml of tetraethyl lead, the decomposition of which gave free ethyl radicals, 0.15, 0.83, 6.4, and 225 molecules of ethylene, respectively, were polymerized for each ethyl radical [9]; in the polymerization of ethylene [10] under the influence of methyl radicals, formed by the decomposition of tetramethyl lead, the use of 0.5 and 7.3% of the latter based on the weight of ethylene gave initiator yields of 5 and 0.59, respectively. A similar

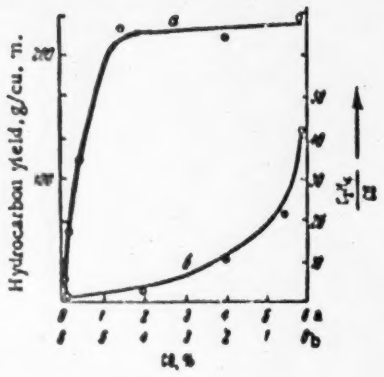


Fig. 1.

dependence of initiator yield on carbon monoxide concentration was observed in the hydropolymerization of olefins; lower concentrations of carbon monoxide corresponded to higher initiator yields, as may be seen from Curve b of Figure 1, which relates to the reaction of ethylene, and from Table 1, where data are presented on the hydropolymerization of ethylene, propylene, and 1-butene. At maximum reaction rate, which occurred for all olefins at 5-6% CO in the initial gas and ratios of hydrogen to carbon monoxide of 6-8, the initiator yield for ethylene was approximately 8, for propylene ~4, for butene ~3, and for hexene 1-2. The reaction rate has a complex dependence on carbon monoxide concentration; in the interval of up to 5-6% carbon monoxide in the olefin-hydrogen mixtures, there is observed a continuous increase in the reaction rate, which decreases with a further increase in CO concentration up to almost complete cessation of the reaction for C_3 and C_4 olefins. The relation of the rate of formation of reaction products and carbon monoxide concentration during the hydropolymerization of ethylene is shown in Figure 1 (Curve a). The heterogeneous-catalytic nature of the hydropolymerization reaction is expressed in the effect exerted by olefin adsorption on the reaction; the reaction proceeds only in the case where there is olefin adsorbed on the catalyst. In work with a gas containing 50% C_3H_6, 25% H_2, and 25% CO, the propylene did not enter into the reaction, nor was it hydrogenated to propane by the hydrogen, although the usual reaction forming hydrocarbons from carbon monoxide and hydrogen was observed. The carbon monoxide, which has a greater tendency toward adsorption than does propylene, blocked the surface of the catalyst, and, with the absence of propylene from the surface, there was no hydropolymerization reaction. The heterogeneous nature of the reaction is also shown by the obtaining of constant yields of hydrocarbons per unit volume of initial active gas when the latter is diluted with nitrogen [11].

TABLE 1

Initial olefin	Concentration of CO in initial gas, %	Initiator yield, %
Ethylene	0.1	44.0
	0.5	22.0
	4.8	8.0
	15—20	4.0
Propylene	5.7	3.7
	6.2	3.7
	11.6	0.7
	13.8	0.4
	15.4	0.2
	18.4	0.1
	22.0	0.0
1-Butene	4.0	2.2
	5.5	2.4
	6.0	1.7
	12.2	0.4
	14.8	0.18

It follows from this that the hydropolymerization of olefins under the influence of carbon monoxide and hydrogen is a heterogeneous-catalytic reaction with a radical-chain mechanism.

Thus, by means of this reaction it has been shown for the first time that it is possible for a heterogeneous-catalytic reaction to proceed by a radical-chain mechanism.

It is entirely probable that the related hydropolymerization process of the formation of hydrocarbon from CO and H_2 also proceeds, in a certain stage, by a radical-chain mechanism. The initial stage of this process proceeds by a radical mechanism (hydrocondensation) with the formation of olefins. With the accumulation of the latter on the surface of the catalyst, hydropolymerization of the olefins begins, proceeding by a chain mechanism and complicated by a number of other reactions, for example, hydrocracking, hydrogenation, etc. The formation of the hydrocarbons proceeds by a complex combination of a radical mechanism with a radical-chain mechanism. In this light, the hydropolymerization of olefins, which begins with the stage of the appearance of olefin, is considered as the concluding part of the complex reaction forming hydrocarbons from CO and H_2.

The identity of their relation to temperature and the great similarity in the nature of the reaction products convince us of the unity of nature of the reactions of hydropolymerization and the formation of hydrocarbons from CO and H_2.

LITERATURE CITED

[1] V. V. Voevdsky, F. F. Volkenshtein and N. N. Semenov, Coll. Questions of Chemical Kinetics, Catalysis, and Reactivity,* Izd. AN SSSR, 1955, p. 4 ff.

[2] Ya. T. Eidus, N. D. Zelinsky and N. I. Ershov, Proc. Acad. Sci. USSR, 60, 599 (1948).

[3] Ya. T. Eidus, N. D. Zelinsky, N. I. Ershov and M. I. Batuev, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1950, 377.

[4] N. D. Zelinsky, Ya. T. Eidus, K. V. Puzitsky and M. I. Batuev, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1950, 647.

[5] Ya. T. Eidus, N. D. Zelinsky, K. V. Puzitsky and N. I. Ershov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1952, 145.**

[6] Ya. T. Eidus, N. I. Ershov, M. I. Batuev and N. D. Zelinsky, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1951, 722.

[7] Ya. T. Eidus, N. I. Ershov and E. M. Terentyeva, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, 882.**

[8] N. I. Ershov, Dissertation, Inst. Org. Chem. Acad. Sci. USSR, 1955.

[9] C. J. Danby and C. W. Hinshelwood, Proc. Roy. Soc., 179, 169 (1941).

[10] P. Cramer, J. Am. chem. Soc., 56, 1234 (1934).

[11] Ya. T. Eidus, K. V. Puzitsky and N. I. Ershov, Coll. Questions of Chemical Kinetics, Catalysis, and Reactivity,* Izd. AN SSSR, 1955, p. 548.

N. D. Zelinsky Institute
of Organic Chemistry
Academy of Sciences USSR

Received April 19, 1957

* In Russian.
** Original Russian pagination. See C.B. Translation.

SUBSCRIPTION PRICES SLASHED ON SOVIET CHEMISTRY TRANSLATIONS

Consultants Bureau is pleased to announce a major achievement in our program to reduce the prices of our cover-to-cover translations of Soviet scientific journals.

An arrangement with the National Science Foundation has made possible reductions of up to 90% in the annual subscription prices of 3 major Soviet chemical journals in complete translation. These price slashes, effective with the first issues of 1957, put these cover-to-cover translations well within the reach of even the most limited library and research laboratory budgets.

The journals affected are:	(Former price)	New price*	Non-profit research and academic institutions*
Journal of General Chemistry (*Zhurnal Obschei Khimii*). Oldest and major Soviet chemical journal—theoretical and experimental reports in organic, analytical and physical chemistry. 12 issues per year, approximately 3600 pages.	$170.00	$90.00	$30.00
Journal of Applied Chemistry (*Zhurnal Prikladnoi Khimii*). All aspects of applied chemical research. Reports from research institutes and USSR factory laboratories. 12 issues per year, approximately 2000 pages.	95.00	60.00	20.00
Bulletin of the Academy of Sciences USSR, Div. Chem. Sci. (*Izvestiya Akad. Nauk SSSR, Otdel. Khim. Nauk*). Research reports in all fields of chemistry, by leading members of the Soviet Academy of Sciences. General, organic, inorganic, physical and biological chemistry. 12 issues per year, approximately 1500 pages.	150.00	45.00	15.00

*Foreign subscriptions—$5.00 higher.

These cover-to-cover translations by Consultants Bureau bilingual chemists are clearly reproduced by the multilith process from IBM cold-type composition. All tabular material, diagrams and photographs are reproduced, integral with the text. Each issue is staple bound and is mailed to subscribers immediately on publication.

CONSULTANTS BUREAU, INC.

227 West 17th Street, New York 11, N. Y.

Telephone: ALgonquin 5-0713 Cable: CONBUREAU NEWYORK